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THE NATURE, ORIGIN AND INTERPRETATION OF THE ETCH FIGURES ON CRYSTALS

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Frontispiece

Natural Etch Figures on Aragonite.

THE NATURE, ORIGIN AND INTERPRETATION OF THE ETCH FIGURES ON CRYSTALS

BY

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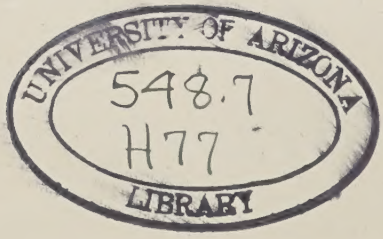

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PREFACE

THIS book [1] represents an attempt to bring together, from a number of different sources, including the author's investigations, the more outstanding facts concerning the nature and origin of Etch Figures as produced by solvent action upon the plane surfaces of crystals. The vast literature of this subject, written for the most part in German, contains much descriptive matter, but with the exception of Baumhauer's classic work, "Die Resultate der Aetzmethode,"[2] there is no concise discussion known to the writer which deals with the theory and application of the Etch Method in mineralogical study. Therefore, this book has been prepared with the idea that a discussion dealing more fully with this topic, which is of growing importance, may be of value to those interested in the application of the Etch Method.

In addition to the theoretical discussion, this volume embodies a description and interpretation of the artificial and natural etchings of ten important minerals, representing six of the thirty-two symmetry classes. The etch figures of these species are fully illustrated by micro-photographs and drawings, thus enabling the reader to gain a better conception of the facial arrangement within the figures and their relation to the symmetry qualities of crystals.

The experimental work, most of which was done during the years 1916 to 1923, has been carried on in the Mineralogical Laboratory of Princeton University, and practically all of the mineral specimens employed in the investigation were supplied

[1] A dissertation presented to the faculty of Princeton University in candidacy for the degree of Doctor of Science, and accepted by the Department of Geology.

[2] Published by Wilhelm Engelmann, Leipzig.

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from the Museum Collection, through the kindness of Professor Alexander H. Phillips, whose ever-ready counsel and friendly criticism have been invaluable in bringing this book to completion.

The author wishes also to acknowledge his indebtedness to Dr. E. T. Wherry of the Bureau of Chemistry, Washington, D. C., who critically read the manuscript and offered many helpful suggestions.

A. P. Honess.

October, 1926.

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INTRODUCTION

THERE probably never has been a period, in the development of mineralogical science, so productive of serious investigation and enlightening results as that of the two or three decades just passed. The ultimate structure of matter, because of the fascination it holds, has become the object of study of many prominent investigators in the fields of physics and chemistry, upon which the science of mineralogy is dependent. The rapid growth of these sciences has made possible new lines of attack and the development of new methods, all of which will eventually lead to a better understanding of the mystery locked for ages within the walls of the crystal. The methods of approach to some of these problems may not in all cases be considered as beyond question, with the result that discordant conclusions may follow. Again, results arrived at during the more primitive days of the science, when reviewed by improved methods and better facilities, may fail to show the expected agreement. Whether the method is at fault or whether the conclusions earlier arrived at were prematurely conceived is a question which can only be answered by further investigation.

The X-ray analysis of crystals has called up some very interesting questions concerning the true symmetry content of certain species, which, upon crystallographic evidence, seem to have been, for the time at least, pretty well settled. It has become very apparent in recent years, however, that data respecting certain crystals, if tested by different methods, chemical and physical, are not wholly consistent; and, as a result, the question arises as to which data are most acceptable, and why the results arrived at by different methods are not in agreement.

The different methods commonly employed to test the classification of a crystal may be summed up under the following heads:

1. Electrical excitation.
2. X-ray analysis.
3. Testing the circular polarization and other optical behavior.
4. Synthetic production of crystals.
5. Development of etch figures and other solution phenomena.

The first three may be considered physical, and the last two, chemical methods. When the five methods are not in agreement in selecting the proper symmetry class, the methods should be reviewed and tested as to whether each in itself is capable of unmistakably indicating the proper class, especially when the hemihedral character is very slight.

The alkali halides, particularly sylvite and ammonium chloride, the diamond, cuprite, wulfenite, apophyllite, chabazite, perovskite, scheelite, natrolite, aragonite, nepheline, rutile, and others, manifest different symmetries when examined by different methods. Concerning the halides, potassium chloride and sodium chloride, there has been much discussion, and many have accepted both as certainly of holohedral character. They exhibit no circular polarization, or pyro-electricity, nor do they exhibit any molecular distortion when examined by X-rays. Potassium chloride, however, if etched with water reveals the facets (931) [1] which correspond to the icositetrahedron; and, furthermore, etching experiments [2] at ordinary temperature indicate that the intramolecular forces of potassium chloride and sodium chloride are different, and that certain lattice regions of potassium chloride are more closely packed, which is rather surprising in view of X-ray studies of these compounds. Yet there seems to be some doubt as to the ability of X-ray analysis [3] to record on a photographic plate such very slight hemihedral distortion

[1] Brauns, Z. Kryst., **13**, 1888, p. 316.
[2] J. Am. Chem., Soc., 1920, p. 3345.
[3] X-rays and Crystal Structure, Ed. 3, 1924, p. 147.

as may be possessed by certain of the doubtful species, or to distinguish between crystal systems where the axial ratios are nearly the same;[4] and at times it is necessary to obtain the crystallographic data before final judgment can be rendered respecting the proper symmetry class. As an example, resorcinol,[5] possessing orthorhombic hemihedrism, may be mentioned. Here, owing to the fact that polarity cannot be detected, the external crystal form is resorted to in order to come to a definite conclusion concerning the presence or absence of a symmetry center. (But even this is not always dependable, owing to uncertainty of polar habit.) In the case of sphalerite, even though polarity be present, and X-rays cannot differentiate between the plus and minus tetrahedral faces, the molecular arrangement may be arrived at without appealing to the polarity property, in which case it becomes no serious obstacle. However, that trouble may arise through application of this method to other than simple crystals, is evidenced in the case of wulfenite and scheelite, a problem in symmetry which is of long standing. According to the results of Dickinson,[6] the positions of the heavier atoms, lead and molybdenum, correspond to holohedral symmetry; consequently, this investigator, knowing from his experiments that the arrangement of the oxygen atoms in wulfenite and scheelite cannot be the same as that in zircon, concludes that the lower symmetry must be related to the oxygen atom, which probably has a dissymmetrical arrangement. The remainder of the problem remains unsolved, however. In the words of Dickinson, "The remaining problem is the location of the oxygen atoms; and here no very satisfactory solution can be claimed." Hence, that wulfenite is of low symmetry may be proven by the X-ray method, but whether or not it possesses a center of symmetry, as does scheelite, is apparently not decided by this method. On the other hand, an examination of the etchings of this mineral points to pyramidal hemihedrism.

[4] Am. Mineralogist, Vol. X., 9, 1925, p. 294.
[5] Science, Vol. 60, No. 1546, 1924, p. 144.
[6] J. Am. Chem. Soc., **42**, 1920, p. 144.

There are other examples which may be cited to show apparent uncertainties in the various methods used. Those of the etch method will be fully treated in subsequent pages; the abnormal pyro-electricity of centrosymmetric crystals, such as topaz, aragonite, barite, etc., has been explained by Beckenkamp [7] as due to polarity of the elementary parallelepipeda of the crystal, accompanied by twinning or grouping of crystal individuals forming a complex whole. That there is a decided tendency for crystals to combine as complex aggregates has long been recognized, and the tendency seems especially strong in low-symmetry forms striving for a higher symmetrical grouping. The external form of such crystals is often very misleading. This so-called pseudo-symmetry is quite common and may be found in twinned unions of individuals whose angles approach those of forms having other symmetry. Chalcopyrite, whose axial ratio is 1 : 0.985 with a sphenoid angle of 108° 42′, approximates the octahedron, whose angle is 109° 28′. The chalcopyrite lattice is then called pseudo-cubical. Other cases of pseudo-symmetry of a different nature may be seen in aragonite, chrysoberyl, witherite, phillipsite, and chabazite; in fact, several of the zeolites possess this property. Chabazite, although rhombohedral in external form, has been shown by Becke [8] to be really triclinic, his measurements of the pinacoids being as follows:

$$(100) : (010) = 83° 42′$$

$$(010) : (001) = 85° 05′$$

$$(100) : (001) = 85° 31\tfrac{1}{2}′$$

These six pinacoidal faces form a pseudo-rhombohedron composed of six triclinic individuals. This, as stated by Jaeger,[9] furnishes a striking example of deceptive grouping, and when it is considered how often these deceptive forms may

[7] Z. Kryst., **44**, 1908, p. 355.

[8] Tscherm. Min. petr. Mitth., **2**, 1879, 391; also Principle of Symmetry, p. 177.

[9] Jaeger, Principle of Symmetry, The Cambridge University Press, p. 177-178.

be encountered it is not surprising that results of the various methods are not in harmony. Such intergrowths as these, along with the superposed lamellar arrangement of Mallard, are indeed instrumental in producing anomalies of different kinds. The experiments of Mallard, Sohncke and von Reusch [10] have shown beyond doubt how circular polarization may be effected in complex crystals individually not so constituted, as illustrated in the salt $(NH)_4LiSO_4$, described by Wyrouboff [11] where intergrown lamellar crystals revealed a rotatory power dependent upon overlapping of the plates. Boracite, according to very extensive etch-figure investigations of Baumhauer ("Resultate", 105–129) at normal temperatures crystallizes with orthorhombic hemimorphic development of the vertical axis. Yet its habit is apparently isometric; and X-ray patterns, according to Jaeger, often show isometric symmetry, which is contrary to the results of both Mallard and Baumhauer. Hence, it becomes clear that often apparently homogeneous crystals are, in reality, complex individuals whose anomalous character may be the source of much discordance in the results obtained.

The following chapters of this book deal principally with the Etch Method as a chemical means of determining crystal symmetry. Although certain conclusions arrived at by the author may meet with some criticism, it has been his intention to present the facts as found. If in so doing he has been able to introduce to a larger group of readers the possibilities of this interesting method, to create a wider interest, and to stimulate honest discussion, the purpose of this small book will have been met.

[10] Jaegar, Principle of Symmetry, The Cambridge University Press, p. 181.
[11] Bull. Soc. Miner. France, **13**, 217; also Principle of Symmetry, p. 181.

THE NATURE, ORIGIN AND INTERPRETATION OF THE ETCH FIGURES ON CRYSTALS

CHAPTER I

HISTORY OF THE DEVELOPMENT OF THE ETCH METHOD

The first scientific application of the etch method seems to have been made in 1808 by Widmannstätten, who observed that characteristic markings may be obtained on polished faces of meteorites through the corrosive action of acids and that the etching so produced is definitely related to the molecular structure of the meteoric iron. He was further able, by means of printers' ink, to reproduce drawings of the so-called "Widmannstätten structure," which were subsequently published.

Eight years later (1816) the results of experimental work on meteoric iron from Brazil were published by Wollaston (Phil. Trans. 265); but to F. Daniell we owe the first application of the etch method to crystal faces. The published results of Daniell's investigations appeared in the Journal of Science of London and Schweigger's Journal during the years 1816–17. Following this there came to notice another article on meteoric iron, "Über die Zeichnungen welche sich bei Auflösung des Meteoreisens bilden," published by Sömmering in Schweigger's Journal in the year 1818. Still another article of similar character, by Schreibers, was published in 1820. Hence, the attention of the early investigators seems to have been directed more to meteorites than to crystals, and not until some years later

did the etch method receive serious consideration as an actual means of crystal classification.

In 1824 there appeared the published work of Moh, "Grundrisse der Mineralogie," wherein he mentioned the differential solution exhibited by rock salt when kept in a damp atmosphere, and the attendant development of quadrilateral etch pits on the cube faces. On saltpeter and alum he made similar observations. Brewster, in 1837, as a result of observations on the etchings of Brazilian topaz, first called attention to the so-called "licht-figuren" which in more recent years have been made a subject of peculiar interest by a few investigators. Leydolt seems to have been inspired by Brewster's discovery, for in his first paper, "Über eine neue Methode, die Structur und Zusammensetzung der Krystalls zu untersuchen mit besonderer Berücksichtigung der Varietäten des rhomboëdrischen Quarzes," published 1854, he remarks (Baumhauer's "Resultate," p. 9): "Brewster hat in einer interessanten Abhandlung gezeigt, dass an von Natur rauhen Krystallflächen von Topaz, Fluszspath, Hornblende, Axinit, Steinsalz, Eisenglanz, Diamant, ferner an den Flächen von Alaun, Fluszspath und Kalkspath, wenn dieselben durch Lösungsmittel oder mit groben Sande rauh gemacht werden, eigenthümliche optische Figuren enstehen. Dadurch aufmerksam gemacht untersuchte ich die bei meiner Arbeit erhaltenen Flächen auch in dieser Beziehung und fand ähnliche Lichterscheinungen, . . . Diese Figuren stimmen immer mit der Gestalt jener kleinsten Theile vollkommen überein so dass man aus der Gestalt auf die Lichterscheinung und umgekehrt schliessen kann." As remarked by Baumhauer, Leydolt seems to have arrived prematurely at the conclusion that the shape of the etching was directly connected with that of the crystal molecule; but later investigation by von Kobell in 1862 and the publication of an important work, "Ueber den Asterismus und die Brewster'schen Lichtfiguren am Calcit," by Haushofer, 1865, proved that no such relation exists. Following Leydolt's first paper, there appeared a second in 1856, entitled, "Ueber die Structur und Zusammensetzung der Krystalle des prismatischen Kalkhaloides"; and from this time on, there continued

an ever-increasing interest in the etching of crystals, as evidenced by the number and character of the publications brought to light, principally through the efforts of German scientists, during the last four decades of the nineteenth century. During this period many notable contributions were made to the theory and application of the etch method, chief among which are the works of Baumhauer, Becke, Klocke, Hamberg, Ebner, Rinne, Traube, Tschermak, Viola, Beckenkamp and Wulff.

The general content of these papers comprises a theoretical study of the etch figure in connection with extensive experimental work, involving the etching of many of the commoner minerals. Such topics as asterism, the importance of the etch figure in isomorphism, the rational or irrational character of the axial intercepts of etch faces, differential solution as exhibited by natural crystals and ground spheres, anomalous etchings, the relation of the etch figure to the crystalline molecule, the conditions controlling the development of the etch figure, and its relation to the symmetry content of crystals are discussed by Baumhauer in a classical work, "Die Resultate der Aetz-Methode in der Krystallographischen Forschung," published in Leipzig in 1894. This represents a very thorough and untiring study of the etch method covering a period of over twenty years, during which there appeared over thirty separate publications by the same author bearing on this line of investigation. This work is the culminating point of Baumhauer's investigations, and, as far as is known to the present writer, is the only complete book on etch figures accessible to-day. Therefore, it is needless to say that Baumhauer's work has been freely consulted in the preparation of this book.

Contemporaneous with the later works of Baumhauer are those of F. Becke, whose investigations of the commoner metallic sulfides, fluorite, and members of the spinel group have given us much valuable information respecting differential solution in crystals, which will be further dealt with in this book.

Traube, in a series of articles, particularly (Neues Jahrb. Min. Geol. Beil. Bd., **10**, 1896, 454) has been instrumental in calling to notice apparent inconsistency in geometrical and

etch figure data, respecting the symmetry of such minerals as cuprite, wulfenite, etc., which are still the source of considerable controversy. Other publications, such as Tschermak's work on the rhombohedral carbonates and sodium nitrate (Min. petr. Mitth., **4**, 1882, 99); Vater's observations on the anomalous etchings of crystals (Z. Kryst., **30**, 1898, 301); three articles, namely, "Über den Aragonit von Sicilien und seine Structur" (Z. Kryst., **28**, 1897, 225), "Uber Ätzfiguren am Gyps" (Z. Kryst., **28**, 1897, 573), and "Homogenität und Ätzung" (Z. Kryst., **31**, 1899, 97), by Viola; the experiments on solubility and etching (Z. Kryst., **22**, 1894, 473), by Wulff; a comprehensive treatise on "Zur Symmetrie der Krystalle" (Z. Kryst., **32**, 1900, 9–48), by Beckenkamp; the work of T. L. Walker on several triclinic minerals (Am. J. Sci., **5**, 1898, 176); and "A Comparative Study of Etch Figures of the Amphiboles," by R. A. Daly (Proc. Am. Acad. Sci., **34**, 1898–99, p. 373), bring to a close the vast literature on etch figures, prior to 1900.

Since that date, a lively interest has been shown in the etching of crystals, and as a result important contributions have been made, leading to a more comprehensive understanding of the method, by such investigators as V. Goldschmidt, F. E. Wright, Koller, Gaubert, McNairn, and others, who have called to attention new possibilities arising from goniometer and projection studies of the etch figure.

In reviewing the literature of etch figures, one is impressed by the leadership of the Germans in this line of investigation, and especially by the work of the two eminent scientists, Baumhauer and Becke, who stand out prominently in the development of this interesting method. Very few English or American mineralogists have been attracted to this field until the last few years, which mark the discovery and development of the X-ray analysis of crystals. This new means of approach to the true molecular arrangement within a crystal has called up several interesting questions, arising from the conflicting data obtained in the study of certain crystalline substances. The etch method, which is considered by many a reliable means of determining crystal symmetry, is not at all times in agreement

with the results obtained by X-ray analysis, and in most cases the apparent discordances have not been satisfactorily explained. Consequently, future investigation, in its attempts to harmonize these discordant results, will improve scientific methods and eventually arrive at the truth concerning the symmetry of the doubtful species.

CHAPTER II

A DESCRIPTION OF THE METHOD EMPLOYED IN THE ETCHING AND EXAMINATION OF CRYSTALS

It is useless to attempt to formulate any set of rules, the strict adherence to which will always secure successful results in the etching of crystals. Each crystal becomes a problem in itself and there are many things to be taken into account, such as the substance, the character of the crystal surface, the crystal form, the transition temperature in some cases, the quality and kind of cleavage, etc. All of these properties may vary in different minerals, and some of them show a very pronounced variation in the same crystal. A solvent which yields excellent results for certain faces of a crystal may prove useless when one is attempting to etch other forms of the same crystal. Occasionally, crystal faces are encountered which reveal a stubborn resistance to solution in different solvents, while other faces of the same crystal may react favorably with almost any of the common acids. The (2131) scalenohedron of calcite may be considered troublesome when subjected to etching processes. The unit pyramid of beryl does not react so favorably with solvents as do other faces of this mineral. Often, a face reveals a very perceptible solvent action, but shows no trace of etch figures, a condition which may or may not change as solution is continued. Very often, in minerals possessing easy cleavage, solution channels rapidly form and cause the crystal to break into laminæ before the etching process is concluded. The basal cleavage in apophyllite may cause a crystal to form solution channels in this direction with a consequent exfoliation to several times the size of the original crystal.

The character of the face and the crystal in general, i.e., its perfection, have an important bearing upon the process used

in etching. The view that extraneous markings and corrosion forms do not influence the etching process cannot be accepted. Better results are always obtained when great care is used in selecting the material for etching, the more perfect crystals being much more desirable than those possessing rough surfaces. As a rule, the smaller crystals serve the purpose better than the larger ones, as those irregularities which so commonly modify the surface are less accentuated in small crystals. Also, surface irregularity may at times appear to alter the outer contour of an etch figure, a fact which should not be forgotten when less perfect crystals are used. However, it is the facial arrangement which is of primary importance, although a symmetrical

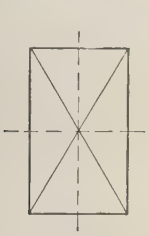


FIG. 1.
Two Planes.

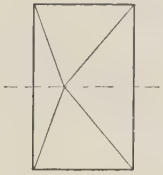


FIG. 2.
One Plane.

FIG. 3.
No Planes.

contour usually occurs with a symmetrical facial arrangement; but an asymmetrical arrangement of faces may occur in a figure which to all appearances possesses a symmetrical contour. (See Figs. 1, 2, 3.) Likewise, certain substances may reveal etch figures that in their very early stage of growth do not appear to show the expected symmetry, which is clearly indicated in the mature figures. This the writer believes to be due in part to the fact that in the early growth stage the hemihedral character, for example, is present, but is less accentuated than in the mature form, and, therefore, may be overlooked. On the other hand, it is possible that the suggestion of Dr. Wherry, elsewhere referred to, respecting unsatisfied bonds at the surface of a crystal, may have a bearing on this point; although it must be admitted that more experimental data would be very desirable.

Furthermore, a figure that is perfectly symmetrical in its

outline and arrangement of faces may, by its orientation upon the face of the crystal, indicate an absence of symmetry planes normal to this surface. An example of this is seen in the symmetrical basal figures of apatite or wulfenite, species which possess no vertical symmetry planes.

A natural surface is usually more desirable for etching than a polished section, for it is impossible to attain, through artificial means, a plane as true as the natural surfaces found on crystals. Hence, in the latter, solution is usually confined to well-scattered points of attack; but in the former, owing to the presence of numerous small pits, it may proceed otherwise, resulting in a corroded surface, which does not show the symmetry so clearly as do distinct etchings. Hence, the development of the etch figure is not controlled by any one factor, but depends upon the solubility of the compound, the nature of the solvent, the character of the face, whether it be of simple indices or unusual in intercepts, etc. Concerning the character of the face, it may be said that the faces of higher reticular density appear to be the ones first attacked and likewise are the faces to yield the best-developed figures. The vicinal faces and striations, when present, should be studied in conjunction with the etchings to insure proper symmetry interpretations.

In choosing material, crystals that are simple and lustrous should be selected, as they will be found to give the best results. These are generally first treated with acids of varying concentrations and temperatures for the purpose of determining which is most suitable. Usually that solvent is employed which does not form an insoluble compound on the crystal surface, as such a compound tends to lessen the solvent action, and is inconvenient to remove. In the case of very insoluble minerals, where acids often cannot be employed, it becomes necessary to use less convenient solvents. Those commonly used are hydrochloric acid, nitric acid, sulfuric acid, hydrofluoric acid, sodium and potassium hydroxides, and a fused mixture of potassium bisulfate and powdered fluorspar. Almost any crystal may be satisfactorily etched by employing several of these solvents, one at a time. Repeated immersions are often necessary, each

immersion being followed by an examination, the purpose of which is to show the stage of etching at which the crystal surface has arrived. If the crystal face after immersion retains its luster and bears very small pits, well scattered, one can feel reasonably sure that such a surface will yield good etchings through continued solution. The binocular is generally used for this purpose when the crystals are opaque or too large to be examined beneath the petrographic microscope. The latter, with nicols removed, is, however, far superior for the study of the etchings when the crystals are of such size and transparency as to permit its use. By repeated immersions of short duration, the etch figures should be allowed to develop to the mature stage, if possible, without becoming intergrown, as this obscures the distinct etch figures, producing hillocks which are often of indefinite character.

The figures having been developed to the desired size, the crystal is then mounted on a glass slide in Canada balsam, with the selected crystal face parallel to the surface of the slide; in this position the figures may be readily studied by transmitted light. If the crystal is too large, as is often the case, it may be placed on the lap and ground parallel to the selected face until sufficiently thin to permit free passage of light, and may then be mounted as before. Several slides of the various crystal forms on a crystal so prepared afford a beautiful study of the symmetry of the crystal and may be conveniently kept for years. The writer has prepared over one hundred and fifty such slides during his investigations, and heartily recommends this procedure to those who are interested in studying etch figures.

Elaborate apparatus is not necessary for the development and study of etch figures, but it is advisable to have available a good petrographic microscope of research type, a binocular capable of 15 diam. magnification, and suitable facilities for photographic work.

Reagents Used in Etching.—A list of the reagents more commonly employed in the etching of crystals follows:

1. Nitric acid.
2. Hydrochloric acid.

3. Sulfuric acid.
4. Hydrofluoric acid.
5. Citric acid.
6. Tartaric acid.
7. Phosphoric acid.
8. Acetic acid.
9. Sodium hydroxide.
10. Potassium hydroxide.
11. Ammonium chloride.
12. Potassium bisulfate—powdered fluorspar fusion.
13. Water.

The common laboratory acids, such as the first three mentioned above, are, of course, very conveniently employed in the etching of soluble minerals. One is not restricted to their use, however, for experiment shows that often very strong solvents, such as hydrofluoric acid or alkali fusions, may be used with very satisfactory results in etching minerals like calcite, willemite, and apophyllite, which are easily soluble. Hard, insoluble species, such as beryl, topaz, tourmaline, and others, are not attacked to any noticeable degree by acids and therefore require alkali fusions. Water-soluble crystals may often be successfully etched by being wrapped in a damp cloth, or even by being permitted to lie exposed to damp atmosphere for a period of days. Some minerals, such as the water-soluble sulfates, may be conveniently treated with mixtures of water and alcohol or with a slightly undersaturated solution of the mineral to be etched.

An Etching Experiment.—To those who are not familiar with crystal etching and the subsequent symmetry interpretation, and particularly to students studying crystallography, the author would suggest the following experiment which can be performed very conveniently during laboratory hours.

Etch figures are usually of definite shape, but vary according to the nature of the solvent, the concentration of the solvent, crystal form, character of the crystal surface, etc. These solution phenomena may be readily witnessed in the etching of quartz crystals. A small specimen of rock crystal ($\frac{1}{4}$ to $\frac{1}{2}$ cm. in diam.),

having the usual combination of plus and minus rhombohedrons and prism, is placed in a platinum dish and covered with concentrated hydrofluoric acid.[1] After two hours' immersion, the crystal is carefully withdrawn, washed in water, and examined beneath the binocular for traces of etch figures. Usually, incipient solution is visible at this time; but if the acid is not sufficiently strong, a longer period of immersion, perhaps as much as six hours, may be required. However, if the acid is placed in a hood and heated over a low Bunsen flame, the solvent action may be hastened so that a crystal may become well etched in one hour's time.

The solvent action having been continued until definite etchings are plainly visible beneath the microscope, a study of the pits can now be made. It will be evident that solution varies with the crystal form and also with direction on any selected crystal face, with the result that the figures of the six prism faces will be alike but will be different from those of either the plus or minus rhombohedrons. One observation that may be made at this point is particularly instructive. It will be remembered that the six faces, usually terminating crystals of alpha quartz, are not of one form, although they appear to be, owing to the fact that these faces are often equally developed. A careful examination will show that the figures on alternate faces only are alike, those on adjacent rhombohedral faces being unlike, indicating that the molecular configuration of the plus or minus rhombohedral planes is characteristic and distinctive. Furthermore, the trigonal symmetry axis *c* is clearly revealed, for faces bearing like etchings turn into congruence after a revolution of 120° about the vertical axis.

An examination of the prism faces will reveal a likeness in the etchings; however, it will be observed, upon turning the crystal about the vertical axis, that the figures on faces 1, 3, and 5 are the reciprocals of those on faces 2, 4, and 6. Hence, the trigonal symmetry of the vertical axis is further demonstrated. Furthermore, the etchings on the prism faces, by

[1] Caution should be used in etching with this acid as it may cause painful injury if spilled upon the hands.

their relative positions, reveal three horizontal digonal symmetry axes, for, by grasping the edges formed by prism faces 1 and 2 and on the opposite side 4 and 5, and turning the crystal, faces 2 and 3 may be brought into view, with face 2 above face 3; rotation of 180° brings faces 1 and 6 around, with 1 above 6, showing the same arrangement of figures as 2 over 3. In a similar way, the digonal symmetry of the other two horizontal axes may be shown by grasping the opposite prism edges formed by faces 2 and 3, and 5 and 6, and likewise the edges formed by faces 3 and 4, and 1 and 6. Careful observation of the rhombohedral etchings during rotation of the crytsal will also reveal a symmetry relation conformable to that observed for the prism etchings.

If the shape of the etch figure itself be now considered, it will be seen that the arrangement of the etch facets is in no case a symmetrical one. The prism figures in the more mature stage are quadrilateral but not divisible by planes of symmetry; nor are the elongated etchings of the rhombohedral faces so divisible. Hence, the crystal faces of this mineral show no symmetry planes. Furthermore, the etchings of one prism face are not mirror images of those on adjacent faces; therefore there are no symmetry planes possible through the prism edges, a fact in accordance with the trigonal holoaxial symmetry established for alpha quartz. It is thus possible to recognize the symmetry of crystals when the diagnostic form, in this case the trigonal trapezohedron, is absent.

Other simple etching experiments may be carried out with calcite crystals or cleavage fragments of Iceland spar. These, when treated with hydrochloric or nitric acid, will show very clearly the dihexagonal alternating symmetry of the hexagonal system. A comparison of these rhombohedral etchings with those of the tetartohedral dolomite furnishes another very instructive study in symmetry.

Method of Photographing Etch Figures.—Not only does the mounted crystal afford a very convenient method of studying and comparing the etchings of crystals, but it likewise makes possible a permanent record of their shapes and orientation

through actual photographs. For work of this kind the Leitz Photo-micrographic Apparatus is well suited. The slide may be at once inserted on the microscope stage (the plane of which is turned vertical) and moved into the light ray from the arc, and the image readily focused on the ground-glass plate. To accentuate the relief and bring out the etchings more clearly, filters of different colors may be used, or the intensity of light be diminished by partly closing the diaphragm. When using the large apparatus, it is probably more desirable to work in a darkened room. However, the "micca" photo-micrographic camera, but recently made available by the Leitz people, can be very conveniently attached to any standard microscope and used to photograph etchings in the laboratory, by either natural or artificial light. The camera attachment can be fitted with either film or plates, and, in the experience of the writer, is a very convenient and inexpensive means of obtaining etch-figure photographs. The magnification may be varied to suit the needs of the investigator, but 180 and 310 diam. have usually been found satisfactory. In some cases, lower magnification may suffice; but, as a rule, the magnification above stated is required to produce a photograph which accurately portrays the inner portions of the figure as well as the outer contour.

The writer has used Wratten M plates, 4 by 5 inches, in the making of many etch-figure photographs, some of which have been previously published in connection with papers on topaz, rhombohedral carbonates, beryl, and members of the dolomite group. He finds such photographs much more interesting than line drawings, which often accompany the published accounts of similar investigations. However, when it is desired to show the relative shapes and positions of the etchings on several important faces taken together, such drawings are of value.

In recent years the reflecting goniometer has come into use as a means of studying the etch figure, and has proven helpful in its reflection of the innermost detailed portions of the pits and the data it supplies as to the definite zoning of etch facets and their subsequent line projections.

CHAPTER III

THE ETCH FIGURE

Definition of Etch Figure.—Etch figures may be said to be definitely shaped solution cavities produced by the momentary or prolonged action of some natural or artificial solvent upon the faces of crystals, the shape and distribution of the cavities being directly attributable to the solvent and to the molecular configuration of the face upon which they occur.[1] Etch figures are usually microscopic in size, but under exceptional conditions they may attain a length and breadth of several millimeters, and be easily discernible by the unaided eye. The action of the solvent upon the face of a crystal is dependent upon the character of the crystal surface, upon the substance, and upon the nature and concentration of the solvent used; and it may be here stated that the faces bounding a crystal may not react in the same manner when subjected to the corrosive action of a solvent. That faces of different forms may show mechanical differences is well known; accordingly, they may manifest different degrees of resistance to chemical action, with the result that the etchings of any one form on a crystal will be constant and characteristic for the faces of that form, provided the solvent remains the same and the etchings have reached the same stage of maturity. The etchings produced by different solvents on the same face may vary to a considerable degree, and some variation in form may be observed with a change in the concentration of the same solvent; but, regardless of the nature of the solvent, or its concentration, the etch cavity invariably reveals the symmetry of the face upon which it occurs, thus precluding any direct relation between the shape of the etchings themselves and the

[1] Thus the term does not include those symmetrical markings or elevations of natural origin commonly observed upon the faces of diamond, topaz, etc.

crystal molecules. The shape of the etchings is more directly connected with intermolecular forces within the crystal, which may be readily overcome by one solvent, causing solution in a given direction, while for another solvent this direction may represent the solubility minimum. One may safely conclude, therefore, that etching experiments are just as definite and reliable, in the story they tell concerning intermolecular arrangement and forces, as are physical experiments, and that the directional and symmetry qualities of a crystal may be just as clearly revealed through chemical as through physical means.

The etch facets, as will be shown later, usually occupy definite zones, a fact of considerable importance in the symmetry interpretation. The faces limiting one of these solution pits may be any one of the forms characteristic of the type in which the substance occurs, or they may be a combination of these forms; and the relative arrangement of these facets with respect to prominent crystallographic directions, and to one another, should be carefully studied. It is well known that the most general form of a crystal class is usually less common than other forms of that class, but it does not follow that this form may not commonly develop as a limiting plane, when the substance is acted upon by a solvent. An illustration of this is the case of apatite, upon which the third-order or characteristic form is seldom observed as a natural crystal face, although it can be produced through solution by almost any of the common solvents; and, in fact, it is the persistence of this form through solution which leads to the discovery of the hemihedrism of this mineral. The base (0001) will always reveal facets of third-order position, no matter what the solvent or its concentration. At least, as far as experiment goes, this seems true. The etchings of the prism faces likewise always develop the characteristic facet which accords with hexagonal equatorial symmetry. And, although there are five other possibilities in the type—etch facets which could develop on the base or the prism in such a way as to reveal nothing but holohedral symmetry—the fact that these never occur uncombined or in the absence of the diagnostic face is certainly of great significance.

It is not always imperative that the most general form of the etching be developed in order to show the symmetry, as in the case of beryl, apophyllite, or cuprite, where any one of the crystal forms may reveal holohedral symmetry. In types of lower symmetry, however, such as that shown by wulfenite, apatite, calcite, willemite, phenacite, and other minerals, the hemihedrism or tetartohedrism could not be shown by etchings which were limited by holohedral facets only. It becomes necessary, then, that those planes which are diagnostic be formed, and experiment appears to show that they are there when their presence is required to indicate the symmetry of the crystal. The fact that the use of a number of different solvents seems not to eliminate this face as a symmetry indicator would suggest that considerable reliability may be placed on etching experiments.

Changes of Etch Figure with Change of Temperature and Solvent.—Baumhauer [2] has strikingly illustrated the change in position of the etchings with variation of solvent. The etchings obtained on the basal face of apatite by means of hydrochloric or sulfuric acid are hexagonal in outline and bounded by third-order pyramid faces, the position of which, with respect to the basal crystalline edges, may vary through a considerable angle, but always passes to an asymmetrical form. Sulfuric acid (sp. gr., 1.836) produced positive third-order pyramidal etch figures, which through dilution of the acid passed to a similar negative form. The following data will serve to emphasize this change:

H_2SO_4 Per Cent	Measured Angle between Side of Figure and Basal Edge
100	+12° 32′ to 14° 0′
60	+ 7° 15′
50	+ 1° 05′
$33\frac{1}{3}$	− 5° 09′
20	−17° 58′ to −20° 7′
10	−14° 29′ to −17° 13′
1	−10° 41′ to −12° 18′
$\frac{1}{10}$	−10° 53′ to −12° 32′

[2] Z. Kryst. **15**, 1889, p. 441.

Dependence of the results upon the concentration of the solvent is also illustrated in Daly's etching experiments (*loc. cit.*) on the amphiboles, where a rotation tendency of the figures was observed on (010) of actinolite with decreasing concentration of the solvents. This fact suggested to Daly the necessity of fixing standard conditions of solution where quantitative data were required.

Even greater changes may be observed in the shape and position of the etchings when a solvent of different chemical nature is used. As an illustration of this, consider the various etchings produced on the second-order prism of willemite by six different solvents, namely, NaOH, KOH, a 1 : 1 mixture of (KOH and NaOH), H_2SO_4, acetic acid, and citric acid.[3] Here a very distinct and characteristic figure is obtained with each of the solvents, and it is noteworthy that each figure corresponds to the same grade of symmetry, a fact which, in the mind of the writer, points unmistakably to the etch method as a simple and reliable means of testing crystal symmetry. This fact of differential solution without change of symmetry has been further illustrated by Burckhardt, who treated tripinacoidal cleavage fragments of anhydrite with different solvents, only to observe that in each case the original cubical form yielded to a new form with no variation in symmetry.[4] Attention may also be called to the experiments on Iceland spar, performed by the writer's assistant, Mr. H. H. Hughes, who successfully etched this mineral with ten different solvents, only to find that the ten different etch figures so obtained were symmetry invariants. As is to be expected, there is a tendency toward greater similarity in the figures produced upon the same face by different solvents than in those produced upon different forms by the same solvent. This fact is at least observable during the etching experiments upon the rhombohedral carbonates, and upon willemite. Investigation has also shown that the nature of the solvent and its concentration are the

[3] Honess, Am. Mineralogist, **2**, May, 1917, p. 58.

[4] F. Rinne, "Crystals and The Fine Structure of Matter," p. 137.

essential factors controlling the shape of the etch figure; the temperature is only subordinate in this respect.

The form of the etching may also change, through continued action of the solvent, from a simple to a complex figure or *vice versa*,[4a] depending upon the substance. This is in harmony with the solution experiments on rock salt made by W. Schnorr and referred to by Rinne in his "Crystals and Fine Structure of Matter," p. 135. The figures in their primitive state are formed by those planes which offer least resistance to the solvent. They are often of very gentle slope and simple arrangement and are usually most successfully developed on faces having simple indices and presumably high reticular density. These earlier-formed etch faces may persist through continued solution, but more often become highly modified by planes of most unusual intercept.

It seems likely that the fundamental crystal forms of simple index are most susceptible to corrosion; this is quite surprising in view of the ready growth of such planes in the solvent. Numerous cases may be cited to show the easy solubility of the base, the unit prisms, and the octahedron and cube, as compared with other less common forms. It must be remembered, however, that even these forms may show variable degrees of solubility, as in the case of the positive and negative tetrahedrons on sphalerite. The base and unit prism of beryl are much more soluble than some of the pyramidal faces; the basal pinacoid of apophyllite is corroded and eaten away after immersion in H_2F_2 for a time sufficient to etch the prism or the pyramid of this mineral. Quartz is exceedingly soluble parallel to its vertical axis, as compared with its solubility normal to this. Experiments on tourmaline spheres by C. Kulaszewski [5] reveal marked solubility of the *C* axis at the antilogous extremity, while the analogous pole is not essentially affected. The base and brachydome of topaz reveal a greater solubility than other less com-

[4a] The basal figures of beryl revealed a multitude of planes, symmetrically arranged around a central pit, which gradually decreased in number as solution continued, until the final etchings revealed but six pyramid faces symmetrically arranged. This change proceeded from complex to simple form.

[5] Ber. Ges. Wiss. Leipzig, **72**, 1920, p. 54.

mon forms found on this mineral, while the scalenohedron on Cumberland calcite [6] is quite unetchable in ordinary acids, compared with the unit rhombohedron or the basal face of this mineral; the difference of solubility of the various forms on apatite is at once noticed upon immersion of this mineral in almost any common laboratory acid, the more common faces etching with greater rapidity although they may not show etch hillocks. Yet it is not an uncommon thing to observe these primary etch faces, fully developed, in the mature figures, showing that, after all, solubility is only a relative term dependent upon conditions of etching.

Growth of Etch Figure.—The modification or growth of the etch figure usually follows two stages: first, the development of the simple primary etch faces representing direction of easiest solubility; and second, the modification of these through the development of secondary etch faces, which appear directly in order of their solubilities and are usually characterized by complex intercepts. In the latter change there is a strong tendency for the secondary faces to arrange themselves in definite zones (the " etch zones " of Baumhauer) [7] and at the same time to approach the position of the etched crystal face, a fact which points to the rationality of the etch faces. The latter process has been called " spreading " by Becke,[8] who designates the etch zone as that zone to which the chief etch faces (Hauptätzflächen) belong, the latter being those faces which offer greatest resistance to the solvent through prolonged action, and which may serve as limiting facets to etchings of all the faces of the crystal. These facets that are limited to definite crystal faces are designated as " Nebenätzflächen," a distinction which investigation proves is quite proper and necessary.

The etch zone of sphalerite is that zone between the cube and the positive tetrahedron, and the faces of this zone retain their glittering appearance after the etching and become covered with individual figures; the other faces, namely, the dodeca-

[6] Honess, Amer. Jour. Sci., **45**, 1918, 201.
[7] Resultate, pp. 15, 19.
[8] Becke, cited by Baumhauer, *op. cit.*, p. 19.

hedron and the negative tetrahedron, lose their luster and are subject to more violent attacks of the solvent than the faces of the etch zone. Here, of course, the polar character of sphalerite is beautifully illustrated in accordance with its unlike development of the poles of the trigonal symmetry axes. The etch zone then offers a greater resistance to solution, when it is considered as composed of the principal limiting facets.

Those crystal faces in which etch hillocks appear, after treatment in the solvent, were later called " Lösungsflächen " in allusion to their greater solubility, by V. Hamberg,[9] who speaks as follows: " Ich habe versucht dieses wort (Lösungsfläche), in seiner ursprünglichen theoretischen Bedeutung beizubehalten, in dem ich diejenigen Krystallflächen, an welchen beim Aetzen die Aetz-hügel entstehen, Lösungsflächen gennant habe." But, since the term " Lösungsflächen " in this sense does not designate the definite crystallographically possible faces only, but all planes which make small angles with the chief solution plane, one may correctly speak of " Lösungszones," or Lösungsregionen,[10] which by Becke were later designated " Aetzfelder " (etch fields).[11]

It has been shown that etch hillocks are really the result of intergrown etch figures and that between the two there is no great difference; but the fact that the crystal faces characterized by etch hillocks and etch figures reveal essential differences in molecular attraction is brought out by marked differences in the solubilities of these faces, the development and explanation of which forms the chief contribution of Becke to the theory of etch figures. It appears, then, that those faces which bear etch hillocks are the planes that oppose least resistance to the solvent and are consequently most rapidly eaten away. However, crystal faces that do not possess etch hillocks may often be designated as easily soluble forms, in the absence of faces bearing hillocks; i.e., certain crystal forms of common occurrence have been considered easily soluble from the stand-

[9] Hamberg, cited by Baumhauer, Resultate, p. 15.
[10] Baumhauer, *op. cit.*, p. 15-16.
[11] *Loc. cit.*

point of momentary etch growth, so that the term, easy solubility, is not confined to corroded faces bearing hillocks, as on simpler crystals these may not always appear.

There is general agreement, however, as to the fact that etch faces are those that offer greatest resistance to the solvent, and lead to proper interpretation of symmetry. Becke and V. Hamberg were wont to disagree on the importance attached to the etch faces; the former emphasized their importance; the latter believed that the so-called " Lösungsflächen " or " Lösungsregionen " were equally significant as a means of determining the solubility ratios of crystal faces, an opinion in which the present writer concurs. The shape of the etchings and their bounding faces most certainly supply invaluable aid in a symmetry interpretation; but the manner in which the various crystal faces react to the solvent, regardless of the symmetry of the etchings, affords valuable data when one is seeking the proper classification of a crystal. An application of this may be seen in calcite, the $(11\bar{2}0)$ form of which, when treated with with HCl in the experiments of the writer,[12] was readily attacked by the acid, forming deep solution channels which extended parallel to the cleavage and could be easily detected long before the figures had attained the mature stage of development—a characteristic much less marked on the unit first-order form. The solution phenomena observed on crystals of polar types are often as valuable as the information afforded by the etch figure itself.

The experiments of Becke, relating to solution phenomena of crystals, are of such importance in this connection that one may well consider the results of his work on several isometric minerals, as summarized by Baumhauer in his well-known treatise.[13]

Upon etching galena with HCl (conc.), the first stages of corrosion were observed on the cube in the form of four-sided pits, the edges of which extended parallel to the crystal edge

[12] Honess, On the Etching Figures of the Dihexagonal Alternating Type, Am. J. Sci., 45, 1918, p. 201.

[13] *Die Resultate der Aetzmethode*, 1894, Leipzig, p. 17, *et seq.*

(001)/(111). Upon application of dilute acid (20 per cent), the cube became covered with etch hillocks (Aetzhügeln) which, being four-sided, corresponded to the dodecahedron. This face gradually revealed modifications, in a position quite near the trigonal trisoctahedron. On the octahedron, triangular etchings appeared, the sides of which were turned to the edge (001)/(111). The bounding faces were those of the trigonal trisoctahedron. The dodecahedron revealed etch channels (Aetzriefen) which extended parallel to the long diagonal of the dodecahedron and corresponded to the trigonal trisoctahedron. Thus the chief etch faces (Hauptätzflächen) on galena lie in the zone of the trigonal trisoctahedron, which may be called the etch zone (Aetz-zone).

The development of certain faces seemed to be controlled by changing concentration, duration of solvent action upon the crystal, and other conditions. Becke attempted to make certain generalizations, showing that the development of certain etch faces was dependent upon concentration and length of time through which solution continued, but he remarks that the differences so influenced are scarcely of more importance than those shown by galena from different localities, or even by different layers from the same crystal.

Becke obtained conformable results upon magnetite, using as solvents HCl, H_2SO_4, and HNO_3. On the octahedron, similar triangular etchings were obtained, the side facets of which were trigonal trisoctahedrons. As in the case of galena, the deepest triangular depressions were truncated by the face (111). With dilute H_2SO_4, the side faces corresponded to the dodecahedron. On the dodecahedral face itself, were formed etchings which consisted of four of the neighboring faces of the dodecahedron and two of the octahedron faces, in addition to solution channels limited by the same faces, which bounded the etchings of the octahedral face. On the cube occurred finally etch hillocks bounded by the same etch faces as are the pits on (111) and (110). When H_2SO_4 was used these hillocks were truncated, either by the cube face or by four faces of the tetrahexahedron, very close to (210) and (310) in intercept.

Becke extended his study to other members of the spinel group, including franklinite, spinel, and pleonast, obtaining results which are in agreement with those for magnetite, the chief etch zone being that of the trigonal trisoctahedron, while the "primäre Aetzflächen" are the dodecahedron and the octahedron.

From his studies, Becke later introduced the idea of "primären and secundären" etch faces, and brought about agreement in terms with the so-called "Lösungsgestalten," primary and secondary, of Ebner. "Primären Aetzflächen" are the faces formed in the earliest stages of solution, and are usually of simple indices; the "secundären Aetzflächen" are those derived through continued action of the solvent and generally have rational but complex intercepts. The fact that one set of figures is derived through modification of the other has led to the formulation of two general laws governing the development of etch figures, elsewhere referred to in this discussion. In order to convey a clearer understanding of these designations, Baumhauer [14] suggests the following example:

"*Sphalerite—Etched by HCl*

"Primäre Aetzflächen":
plus tetrahedron and cube
"Secundären & Hauptätzflächen":
plus trigonal tristetrahedron
"Nebenätzflächen":
On (001) minus trigonal tristetrahedron
On (111) plus hextetrahedron
"Aetz-zone":
(111), (001)."

Linnaeite (Co_3S_4) had been investigated by Baumhauer [15] in 1874, and his results were in harmony with the more recent observations of Becke.[16] Both investigators remarked the similarity

[14] *Op. cit.*, p. 20.
[15] Sitzungsber. Bayr. Akad. Wiss., 1874, 245.
[16] Min. Mitth. 7, 225, 1885.

in etchings between this species and magnetite when acids were used; with KOH its behavior was very different. On the (111) face triangular figures were produced which assumed a turned position with respect to those obtained by acids. The bounding faces lay in the zone of the most general form. Sphalerite and galena behaved very much like linnaeite when acids were employed as solvents, indicating a strong affinity of acid for sulfur.

It is to be observed here, then, that the cobalt sulfide reacts with acids in a manner similar to magnetite, yielding the same etch zone, but that the KOH solvent causes a vast difference in the formation of the figures, yielding an entirely different etch zone. This fact points to the conclusion that the directions of greatest and least solubility may change with a change of solvent, and indicates the individuality of solvents and their reaction upon the molecular network of a crystal. The unlike positions of the atoms that are first attacked in the crystal molecule is suggested by Becke as a possible cause for the change, and he infers that the crystal molecules of linnaeite are so constituted that the chemical molecules which compose them turn their metal atoms to the dodecahedral face. Becke emphasizes the fact that change in the solvent is accompanied by decided change in the etchings only when there is a pronounced chemical difference in the solvents. His statement is as follows: "Der Erfolg der Aetzung wird bei einer Aenderung des Aetzmittels dann ein anderer, wenn durch das neue Aetzmittel ein ganz anderer chemischer Process hervorgerufen wird." [17]

It is true that many minerals exhibit a very decided difference in their behavior toward the common laboratory acids as compared with the alkali hydroxides, and even the results of H_2SO_4 as against those of HNO_3 and HCl often reveal distinct differences. The figures produced by acids on the prism of willemite, and on the prisms of apophyllite and apatite, in each case fail to show such marked dissimilarity as when a comparison is made between acid and alkali figures produced on similar crystal faces. Maximum solution is not confined to any one direction for all solvents, any more than a given crystal face

[17] Baumhauer, Die Resultate der Aetzmethode, p. 20.

may be expected to dissolve with the same rate of speed regardless of the solvent brought to act upon it. The (111) pyramid and (100) prism of apophyllite may be beautifully etched by dilute H_2F_2 in twenty minutes' time, but these faces when immersed in fairly strong H_2SO_4 fail to respond to the action of the acid even to the slightest degree, maintaining a perfect luster and the characteristic facial markings after many hours' immersion. The base of apophyllite is completely destroyed by such treatment, the acid eating its way to the central core of the crystal, causing it to fall to pieces. The process of solution depends upon the chemical constituency of the crystal faces and upon the electrically charged atoms of the solvent; if there is no attraction, there is no solution in that direction. The suggestion of Ichikawa [18] may well be considered in this connection. A quartz crystal subjected to the action of H_2F_2 develops a groove on each positive edge of the prism; the negative edge remains untouched; this is explainable on the basis of molecular attraction as follows:

The positive ions Si occupy prominent positions on the positive prism edge in the region of the positive lateral axes; these ions are attacked by the acid with the negative ion F. Naturally etched crystals of quartz show a groove on the negative edge with ions O. May it not be suggested that some solvent, as Na or K solution, with positive charge, acted as the solvent? The fact that the base of quartz is attacked equally is explained by a condition of neutrality maintained among the molecules.

Becke's experiments on magnetite spheres revealed marked differential solution. The directions of least solubility formed edges and corners, while a flattening was apparent in the direction of maxium solution, which in this case was the normal to the cube.

Upon etching pyrite with acids, the cube faces were found to possess etch figures bearing faces of the positive pyritohedron with an intercept lying between (102) and the cube. The pyritohedron faces revealed pits lying in the zone $(102\text{–}\bar{1}02)$, but their slope within this zone may change with conditions of

[18] Am. J. Sci., **39**, 1915, p. 470.

etching. The octahedron under similar conditions revealed etch hillocks and assumed a dull appearance. The faces of the dodecahedron and negative pyritohedron likewise showed etch hillocks. Thus the zone containing the faces (102)—(001)—($\bar{1}$02) stood out as the " Hauptätzzone " (chief etch zone) when acids were used on this species.

Different results were obtained when alkalies were used as the solvent. The octahedron, which with acids had been covered with elevations and was characterized by dull luster, now became bright and afforded most distinct etch figures. On *P* (102) there appeared, at the same time, etch figures and etch hillocks, while the cube and dodecahedron became dull and covered with elevations; the octahedron became the primary etch face, but no definite etch zone was observable. The faces of the etch zone (102) and the cube offered greatest resistance to solution. The crystal faces arranged in order of decreasing resistance to solution are: cube, plus pyritohedron, dodecahedron.

Becke also made a very thorough study of fluorite; the results he obtained with HCl may be summarized as follows:

The primary etch faces (primäre Aetzflächen) are the cube and the octahedron; the primary etch zones are the " Ikositetraëder," and the trigonal trisoctahedron zones. The cube faces were etched with four-sided figures, formed of the " Ikositetraëderflächen," while the octahedron revealed, in addition to triangular pits formed of similar faces, six-sided etchings formed of both " Ikositetraëdron " and trigonal trisoctahedron faces. The factor which determines the predominance of one or the other kind is the concentration and temperature of the acid. Further, he remarks that the relationship which exists between the etch faces and the faces of rational intercept is not so obvious as is the case with other minerals, and consequently fluorite is not as complete in the information it affords as a result of the etching action; and those faces which on the other species were known as " Hauptätzflächen," because of their uniform identity and general distribution over the crystal, may not be so designated in the case of fluorite, owing to lack of identity in form. Best results were obtained by the use of alkali carbonates; the

primary etch zones so produced comprise the zones of the tetrahexahedron and the trigonal trisoctahedron, while the dodecahedron and the octahedron are the primary etch faces (primäre Aetzflächen). It follows, then, that the octahedral faces are primary for both the acid and the alkali solvents, and likewise in both cases the trigonal trisoctahedron zone becomes an etch zone while the tetrahexahedron and the "Ikositetraëder" change places.

The general conclusions to be drawn from Becke's experiments are as follows:

(*a*) Solution proceeds with the same rapidity in directions that are crystallographically equivalent, but varies with directions crystallographically unlike. These variable solubility directions, of course, govern the form and position of the etch figure.

(*b*) Directions of maximum and minimum solubility may change with the solvent, as a result of which, first one, then another of the primary faces may represent minimum or maximum solution.

(*c*) The change in the succession of faces according to solubility is attributable to the position of the atoms in the molecule. As an example, Becke suggests, from his experiments on fluorite, that the calcium atoms have greater influence upon the dodecahedron face, while the fluorine atoms turn more to the faces of the cube.

The growth of etch figures may take place instantaneously, and through only a few seconds' immersion in a suitable solvent, etchings may assume a final, definite form. On the other hand, the action of the solvent may be so retarded as to require many hours' contact with the crystal face before definite etch figures appear. Many good illustrations of rapid growth may be cited: The Cumberland calcite,[19] upon immersion in 10 per cent HCl for only a few seconds, revealed distinct etchings on the unit

[19] On the Etching Figures of the Dihexagonal Alternating Type, Am. J. Sci., Vol. XLV, 1918, p. 201.

rhombohedron, which by comparison with retarded etchings or other forms gave a distinct clue to the various crystal forms and consequently to the crystal symmetry. Immersion of smithsonite for only two seconds in HCl was sufficient for the development of distinct etchings. The second-order prism of willemite,[20] after a few seconds' immersion in alkali hydroxide, reveals distinct etchings, which may differ from figures produced by retarded growth in a weaker solvent of the same chemical constituency.

The rapidity of growth apparently has no influence upon the perfection of the figure produced, but it may influence its shape. Etchings of exceedingly rapid growth may be in every way as complete and representative in arrangement of faces as those formed through retarded action of the solvent. In fact, Goldschmidt and Wright [21] are inclined to favor violent, rapid action of the solvent upon the crystal face, and Miers in his experiments on calcite remarks that larger and more perfect etchings are obtained by a stronger corrosive. In the experience of the writer, this question rests wholly with the substance to be etched, the face, and the chemical character of the solvents. Excellent results may be obtained on easily soluble minerals through violent action of a strong solvent for a brief period of time; but equally good results may be obtained through long-continued action of a weak solvent. Just as satisfactory results were obtained on willemite with alkali hydroxide as with dilute acids; and the writer ventures to add that, in the majority of cases, satisfactory results may be obtained by either method, although experience has shown that long-continued solvent action has usually resulted in very large, definite etchings.

Likewise, there are many examples of retarded growth, some of which have come under the writer's observation and may serve as illustrations here: The base of Cumberland calcite is beautifully etched after twenty minutes' immersion in cold 25 per cent citric acid, with figures which differ from those pro-

[20] A Study of the Etching Figures of the Hexagonal Alternating Type of Crystals, Am. Mineralogist, **2**, May, 1917, p. 58.

[21] Neues Jahrb. Min. Geol. Beil. Bd., **17**, 1903, p. 379.

duced upon the same face by hot concentrated citric acid, acting for only three minutes. Magnesite, boiled for half an hour in dilute HCl, revealed very distinct etchings on the rhombohedron. Apophyllite crystals, having lain forgotten for days in a platinum dish filled with very dilute hydrofluoric acid, were found to be beautifully etched with most unusual figures, a fact rather suggestive of the conditions under which natural etchings are formed, when it is remembered that etch figures of natural origin are often exceptionally large and well defined, in many cases far surpassing any attempts at laboratory production. Instantaneous and retarded [22] etchings, terms employed by Ebner, constitute the end members of a series of forms which may be distinguished by different velocity of development, and which are related through transition.[23] Consequently, it may be difficult to differentiate these figures. The figures above mentioned, however, as being developed through rapid or delayed solvent action are not strictly comparable to those of Ebner, which are related through evolutionary changes.

Interpretation of Etch Figures.—As a result of transitional changes in the growth of etch figures, it follows that the face of a given crystal form may reveal unlike figures, and likewise unequal distribution over the crystal face; but the figures are almost always of definite crystallographical direction. (Anomalous solution channels and the so-called beaks, such as often occur, need not be considered here.) Anyone familiar with the etching phenomena observed on crystals has, time and again, had his attention directed to what is apparently an evolutionary change during the growth of the etch figure. The etching in its primitive state need not have the same shape or orientation as the mature figure; it may be, and very frequently is, essentially different. The change may be one from simplicity to complexity with attendant straightening of boundary lines, but not necessarily so. The figures produced on the base of topaz

[22] The terms "instantäne" and "retardirte" were introduced by V. v. Ebner (Sitzber. Akad. Wiss. Wien, 1884 (89), 368; 1885, 91, 760), to classify etch figures on a basis of time allotted for their development.

[23] Baumhauer, Die Resultate der Aetz-methode, Leipzig, 1894, p. 4.

by potassium bisulfate—fluorspar fusion [24] serve to illustrate this change. (See photo 78).

Often the diamond-shaped etchings produced on the (100) prism of apophyllite by dilute H_2F_2 are entirely different in their earlier stages of growth (see Photos, 1, 2, 6). Here one may see the development of bilaterally symmetrical etch figures from primitive pits which in some cases are apparently asymmetrical. The very first attack of the acid may give rise to the formation of simple, irregular, rounded depressions, slightly elongated normal to *C*. These gradually broaden through the development of two gently sloping faces of the zone *a/c*. These faces continue to grow and are by far the most prominent on the figure midway between primitive and mature developmental stages. Immediately following these there are developed four definite triangular faces of rather steep slope, two lying symmetrically on either side of the prominent etch faces of the zone *a/c*. To these four faces the resultant etch pit owes its shape (which with age becomes decidedly more angular). In the earlier stages of growth these faces may not shape up as readily on one side of the figure as on the other, and consequently may give the impression of a lower symmetry; but, through continued solution under normal conditions of growth, the resultant etch figure becomes a perfectly symmetrical form, limited by four triangular faces, coincident at a central point, representing the pit of the figure, whose elongation is now at right angles to that of the primitive figure, and the prominent faces of the zone *a/c* disappear entirely. This is the stability solution form.

After the etching has reached this stage, solution may be continued indefinitely without any change in the etch figure, except an increase in size, which ultimately results in intergrowth and corrosion hillocks, often followed by a second generation of etch cavities. It must not be inferred, however, that the etchings of the prism (100) of apophyllite, as produced by dilute H_2F_2, always undergo this change. They may or may not form in this way. Often the first attack of the acid reveals minute pits which under high magnification are distinctly

[24] The Etching Figures of Topaz, Am. Mineralogist, **6**, 1921, plate 3, p. 76.

diamond-shaped; consequently, their growth is simply increase in size. Later in the etching process, however, the primitive figures of rounded form may appear on the same face and pass through the transitional stages described above. Thus, it is evident that there are two distinct groups of etchings: Those composing the first group (*a*) are the result of momentary solution; their primary etch faces lie in the zone *a*/*c*; and by their arrangement they *may not in all cases appear to represent the true symmetry of the crystal face upon which they occur.* The second group (*b*) comprises those figures which have been produced through continued action of the solvent through a longer period of time, the primary etch faces of which lie in the zone of the prism (100) and pyramid of the first order. The figures are distinct and of definite orientation, and reflect the symmetry of the crystal face upon which they appear.

Between the two groups there is an observable evolutionary transition, the etchings of group (*b*) being derived through continued solution from those of group (*a*). Just as interesting changes may be observed on the unit pyramid of apophyllite, when etched with H_2F_2; on the base of topaz when treated with potassium bisulfate-fluorspar fusion, or on the (011) form of celestite or anglesite when etched with dilute nitric acid. In fact, many crystals when etched under favorable conditions may show transitional figures which should be looked for and correctly interpreted. For a more detailed account of the developmental changes involved in etch figure growth, one may well consult McNairn's "The Growth of Etch Figures."[25]

This undoubtedly raises a question as to the proper interpretation of etch figures. Conflicting reports concerning the etch figures of certain crystals may in some instances be traceable to this cause. Pelikan [26] in his investigation of Nordmark diopside seems to have misinterpreted his etchings, which led him to arrive at erroneous conclusions concerning the symmetry of this mineral. However, Baumhauer, after examining these specimens, concluded that the dissymmetrical forms were either

[25] Trans. Roy. Can. Inst., 1916, pp. 231–268.
[26] Min. petr. Mitth., **16**, 1896, p. 1.

immature, in which case they would become symmetrical through continued solution, or else were the result of intergrowth of primitive and immature etchings. Both the immature and the intergrowth forms may commonly be observed during the process of crystal etching. The writer ventures to suggest that some similar misinterpretation may be found to account for the divergence of opinion among various investigators respecting the etchings of some of the alkali halides. In this connection, also, it is well to point out that the growth of the etch figure is largely a replacement or substitution process, whereby the more soluble faces yield to the insoluble, causing a very material change in the character of the pit. Consequently, it becomes evident that age is a very important factor governing the form of the etch figure.

The writer has often observed doubtful etchings, on calcite, beryl, and other minerals, which through prolonged solution resulted in accordance with the expected symmetry. Tutton [27] remarks in his discourse respecting the probable misinformation arising from etch figures, " Similar evidence in the case of rock salt has proved to have been misleading for more prolonged action of a solvent resulted in holohedral etch figures being obtained."

In view of the above data, it is very evident that etchings of varied character may be found upon the same crystal face, concerning which one may well inquire as to the correct method of interpretation. The writer believes that those etchings which assume a stability shape through prolonged solution reveal the true symmetry of the crystal face, and that immature etch pits cannot in every case be relied upon to show correctly the symmetry content. Nor can a mature etching always be depended upon to reflect the symmetry of the face, regardless of the character of the crystal face. Natural etchings and solution channels, striations, complex interpenetration twinning, vicinal faces, etc., may affect the appearance of the etch figure. If this were not the case, all crystals of the same substance, if

[27] Tutton, Cryst. and Pract. Cryst. Measurement, **1**, 1922, p. 677, by permission of The Macmillan Co.

of the same habit and equal purity, would be expected to etch alike with equally satisfactory results. That such is not the case is readily observed when one attempts to etch large, rough crystals. To be sure, there is very little difference in the solution phenomena exhibited by similar crystals of the same substance, when once the crystal surface has been destroyed, but the writer does maintain that unless the surface of the crystal face to be etched is fairly free from such irregularities as those mentioned above, satisfactory etch figures cannot be produced. Instead of attacking the crystal face at well-scattered points, giving the pits an opportunity to develop individually, the solvent will attack in such a manner as to destroy the face without the slightest evidence of definite etch pits, producing a corroded surface covered with elevations and depressions which are not in the strict sense to be spoken of as etch figures. However, during the discussion of the growth and distribution of etch figures, it will be shown that surface irregularities, when not accentuated, serve as centers of solution resulting in etchings.

Distribution of Etch Figures on Crystal Faces.—The fact that etch pits do usually confine themselves to well-scattered points over a crystal face, provided that face is not immediately removed by solution because of its imperfection, seems to point to one of two causes, either a slight rupture or other irregularity of the molecular plane forming the surface, or differential cohesion within the crystal, i.e., either extraneous or inherent circumstance. However, no explanation which would adequately account for the distribution of etch pits over the crystal surface seems to be accessible. Baumhauer [28] failed to see any relation between surface fracture and pit distribution, and mentioned, as a possible cause, inhomogeneity (p. 111), which probably has the same significance as Retgers' "Schwache Stellen." But this does not account for the fact that cleavage plates usually meet etching requirements better than exterior crystal faces, a fact noted by Baumhauer himself [29] and further confirmed by

[28] Z. Kryst., **30**, 1899, p. 109–110.
[29] *Op. cit.*, p. 3.

Daly.[30] McNairn,[31] in his discussion of this point, seems to have pretty well proven that currents, according to the Goldschmidt theory, cannot in all cases be responsible for the etch pit; and that foreign bodies, such as dust, on the surface or inclusions within the crystal have been observed to fail as a means of explanation, although it has been pointed out by Gaubert that coloring matter in a crystal modifies the resistance of the face to the solvent, as exhibited by crystals of phthalic acid ($C_8H_6O_4$) when colored by methylene-blue and malachite-green; etching develops more rapidly on those crystals containing methylene-blue. A somewhat similar illustration of the disturbance of growth equilibrium was noted by Rinne, who observed that the addition of a trace of a certain dye produced an irregular mass of calcium sulfate sheets instead of well-formed crystals such as those deposited from pure solution. That fracture of the crystal surface may in some cases be responsible cannot be denied, for, according to the experiments of the writer, such irregularities have been known to cause immediate solution at these points, and, furthermore, to serve as the starting points of numerous solution channels. Incipient cleavage may often be indicated by well-defined rows of etch figures, which ultimately coalesce to form deep solution channels parallel to prominent cleavage directions. Often, on faces parallel to primary cleavage, as, for example, the base of apophyllite, there have been observed solution channels extending in directions at 90° to one another as if to indicate a secondary cleavage direction. It is evident that both fracture and cleavage may to some extent govern the distribution of etch pits.

Probably one of the most important factors, however, is the molecular arrangement, whether this be due to vicinal hillocks, striations, twin contacts, facial rupture, or some other cause. Inasmuch as crystals reveal differential solution, such irregularities permit of attack by the solvent in different directions; and perchance one of these is the direction of easy solubility, which is, let us say, more susceptible to solution than the crystal

[30] Proc. Am. Acad. Sci., **34**, 382.

[31] The Growth of Etch Figures, Trans. Roy. Can. Inst., 1915.

face itself. If we assume that a given crystal face, cube of NaCl, for example, is a perfect plane of molecules, then each point in that plane, according to the laws of crystalline matter, should offer equal resistance with every other point for any given direction. Then, if the solvent is perfectly uniform in concentration and temperature and cannot act in any direction except that normal to the crystal face, it is difficult to see how scattering etch pits may arise. One wonders how "weak attachments" between adjacent crystal molecules, as suggested by McNairn, can so occur in a homogeneous crystal unless it be in a regular, orderly fashion. Are we to understand that these regions of "weak attachment" are heterogeneously distributed through the crystal? If so, how can the physical properties be uniformly directional? To what cause may these regions of "weak attachment" be due? One can readily understand how regions of enfeebled cohesion may arise through enclosure of foreign material; in fact, Beckenkamp [32] has suggested that foreign admixture may affect crystal habit, and likewise, by occupying certain positions between the crystal molecules, may modify the electrical polarity and ultimately the manner of solution upon which the etch figure is dependent. But this explanation, according to McNairn, does not seem to be completely in harmony with experimental results, and therefore cannot be regarded as the only explanation.

The writer believes that it is a question of maximum and minimum solubility arising from surface irregularities of different kinds, and in his opinion the assumption that very local alteration may in rare cases be responsible is not beyond reason. If slight elevations occur on the surface of a crystal face, which appears to be quite insoluble, it is very probable that directions normal to some of the faces bounding these hillocks will represent directions of maximum solution; at least, it can be asserted that solubility parallel to some of these directions will be greater than that normal to the crystal face; in which case solution would begin at this point.

[32] Z. Kryst., **32**, 1900, p. 32.

A brief consideration of the diagrams below may serve to clarify the author's idea (see Fig. 4).

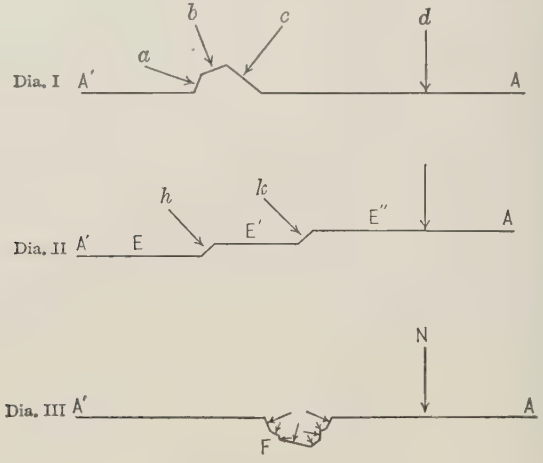


FIG. 4.

Three conditions may commonly prevail:

(*a*) Irregularity of crystallization as shown in Diagram I. Such surface markings may commonly be observed on many crystals, their origin not being definitely known. It should be noted, however, that these hillocks are not etch phenomena.

(*b*) Striated surfaces produced by oscillatory growth between two forms (see Diagram II). These may be exceedingly small or of appreciable size and distinctness.

(*c*) A cavity in the face of a crystal, which may be a primitive, natural etching, a cavity produced by primary processes of crystallization, or a rupture of the crystal surface through mechanical means (see Diagram III).

Considering Diagram I, the line $A'A$ may represent the surface of the crystal face to be etched. The line *d* represents the direction of difficult solubility, that normal to the face. The corrosive may then select any or all of the lines *a*, *b*, *c* as a means of attack, as these represent normals to the faces bounding the elevations, and it is not likely that all of these are equally resistant to line *d*. Consequently, corrosive action may start at this point.

In Diagram II, E, E', E'' represent the surface to be etched. But through oscillatory growth the faces to which normals h and k are drawn may prove to be those of greater solubility and consequently a means of attack. That the surfaces E, E', E'' may be etched seems probable in case certain solvents are used, as it is not understood that these are perfectly plane; but the primitive figure always arises where solution is most easily effected.

In Diagram III a rupture of the surface is shown at F. Such a cavity affords an excellent means of attack, as directions of easy and difficult solubility are alike exposed to the corrosive. However, for certain solvents the direction normal to the face itself (line N) may prove to be one of maximum solubility, in which case there would be no excessive solution noticeable at F.

This condition may hold for a given solvent, but not necessarily for all solvents, as the directions of greatest and least solubility may change with a rather decided change in the chemical character of the solvent used. This fact was pointed out by Becke, and later forcibly illustrated by Kemter in his experiments on celestite. New points of attack, which proved impervious before the change, may be selected. It would be interesting to apply different solvents to adjacent planes of cleavage, as suggested by McNairn, and observe whether this "weak attachment" remains stationary in position for all solvents or whether it appears at new points over the faces. If these regions of "weak attachment" are subject to change with variation in the solvent, it may be that the ideas of McNairn and of the writer eventually lead to the same conclusion.

The writer does not maintain that any *one* of these causes operates alone to explain the distribution of etch figures on a crystal face; but it seems very probable that, taken together, they become an important factor. This may explain why, in certain cases, unusually fine cleavage faces serve better for etching than the less perfect exterior faces of the crystal. It further suggests an explanation of the fact that the very small and more perfect crystals usually exhibit very fine etchings, which are less abundant and more widely scattered than are those developed on crystals possessing less perfect exteriors.

Nature of the Etch Pit.—The factors governing the growth of the etch figure having been considered, it may be well to dwell briefly on the nature of the etch pit itself, its usual habit, and also anomalous etchings, which are often attendant.

Whether or not the faces bounding an etch figure conform to the Law of Rationality of Indices has long been a subject of discussion. Some of the earlier investigators were inclined to the idea that etch faces were of simple index. Leydolt [33] assumed that such faces were of simple, mathematical ratio, but was not able to confirm the view through actual measurement. Sohncke,[34] in describing the etchings on the cube faces of rock salt, suggested the following positions for some of the more prominent faces of the etchings: (910) and (10–1–0) of the tetrahexahedral zone; but, he added, "nach den vorgenommenen Messungen ist es jedoch wahrscheinlich, dass die Aetzfiguren am Steinsalz gar nicht auf einen bestimmten Pyramidenwürfel bezogen werden können." F. Klocke,[35] in his experiments on alum, found the intercepts to vary with different crystals in a manner which could not be attributed to error in observation. Some of the faces measured by him correspond to the following: (15–1–15), (30–1–30), (778), (557), and others vary between these forms. Kemter [36] reported a number of unusual etch faces occurring on celestite after treatment with nitric, hydrochloric, and sulfuric acids. These were as follows:

Facets Identified

Form Etched	HNO_3	HCL	H_2SO_4
(001)	(118)	(hol) only distinct	(hol)
(010)	(OKl)	(061)	(1–27–25), (095), (021)
(100)	(5–4–0), (15–0–1)	(610), (10–0–1)	(hkl) not determ.
(110)	(9–11–0), (19–16–0)	— not given	(992), (340), (540)
(011)	Not determ.	— not given	(1–36–33), (0–12–7)

[33] Baumhauer, Resultate, 1894, p. 12.

[34] Neues Jahrb. Min. Geol., 1875, 941; also Resultate, p. 12, Sohncke cited by Baumhauer.

[35] Z. Kryst., **2**, 126.

[36] Ber. Ges. Wiss., Leipzig, 72, 1920, p. 56.

Solution experiments on polished sections with the same solvents gave rise to the following facets: (430), (410), (110), (102), (506), (24–0–5), (0–1–17), (2–3–18), (3–4–14), (3–10–0), (650), (6–13–26), (0–26–11), (9–36–16), (70–1–0).

It is to be noted that, while many of the above indices approach very closely the simple forms commonly observed on crystals, there are very few that are actually recorded as definite crystal faces. The unusual character of etch facets was also remarked by Kohlmann [37] in his observation of the natural corrosion of Brazilian beryl. Owing to the exceptional size and perfection of the etch pits, this author was able to make casts by filling the cavities with sulfur to which had been added a little iodine, a method formerly employed by Brauns. The measurements corresponded to the following etch faces: (11–0–11–2), (1010), (24–0–$\bar{2}\bar{4}$–5), (3031), (3–3–6–10), ($\bar{3}$364), (11$\bar{2}$1), (0001). Petersson [38] recorded the etch face (20–1–$\bar{2}\bar{1}$–20) as of natural origin on beryl from Mursinsk. Brauns,[39] by carefully covering smooth cleavage fragments of rock salt with paper, was able to expose the mineral to the damp atmosphere for a period of two months, with the result that he obtained beautiful etchings bounded by tetrahexahedral facets corresponding to the following series of intercepts: (21–2–0), (10–1–0), (910), (33–4–0), (810), (29–4–0), (710), (25–4–0), (610), (23–4–0), (11–2–0), (21–4–0), (510), (920), (410), (15–4–0), (720). By changing the character of the solvent, different facets were developed, but always of this zone.

Penfield [40] calculated the following indices from measurements of naturally etched crystals of Mt. Antero beryl: (36–24–60–5), (6–6–$\bar{1}\bar{2}$–1), (2021), and concluded that these faces were really solution remnants of larger beryl crystals. Therefore, from a consideration of the measurements obtained by several investigators, the unusual character of etch facets is at once recognized. Although beneath the microscope their

[37] Z. Kryst., **49**, 1911, p. 389.
[38] Z. Kryst., **19**, 1891, p. 99.
[39] Z. Kryst., **19**, 1891, p. 306.
[40] Z. Kryst., **20**, 1892, p. 491.

position may often suggest that of a simple ratio, actually it is very different in most cases. That such faces possess rational indices has been confirmed by Brauns [41] in his etching experiments on rock salt; Becke [42] had previously arrived at a similar conclusion, calling attention to the modification of the primary etch faces by those of complex intercept, this being effected by change in concentration of the solvent in the innermost parts of the pits. It may be assumed, therefore, that the faces bounding an etch figure are usually planes of rational, though not simple, intercept, lying in definite crystal zones analogous to vicinal faces. It is well known that the so-called vicinal faces are of greatest importance in displaying the true symmetry of a crystal by virtue of their positions representing planes peculiar to certain types, and this fact, in view of the recognized similarity between etch and vicinal faces, at once suggests the importance of the etch figure in a similar capacity.

That etch faces may have curved surfaces seems entirely possible; but whether they are as common in occurrence as some writers assume may well be doubted. V. Goldschmidt and F. E. Wright,[43] from an elaborate study of the etchings of calcite, involving the use of the two-circle goniometer, conclude that etch pits are bounded by curved surfaces which in a measure prohibit a thorough study of their relations. In this connection they say, " Die Ätzfiguren sind von krummen Flächen begrenzt. . . . Wegen der Complicirtheit dieser krummflächigen Gebilde bietet nur deren polares Projectionsbild genügende Übersichtlichkeit zum Studium der Beziehungen." Gaubert [44] concludes that corrosion figures with curved surfaces, like those on natural crystals, may be produced through variation in the composition of the surrounding medium.

Theoretically, of course, a crystal cannot possess a curved face, but it is well known that many minerals do exhibit rounded surfaces as a result of vicinal growths, and, since the numerous

[41] *Op. cit.*, p. 306.
[42] *Op. cit.*, p. 306.
[43] Neues Jahrb. Min. Geol. Beil. Bd., **17**, 1903, p. 368.
[44] Compt. rend., **143**, 1171–72.

etch facets of a corroded crystal, taken together, correspond to a negative crystal of that substance, there must be a direct relation between the facets bounding a figure and the molecular arrangement of the face upon which it occurs, and doubtless the same causes that are instrumental in the development of natural crystal faces are operative in the growth of etch facets. It has often been repeated that a crystal face during formation is dependent upon two forces,[45] the interatomic force working within the crystal and striving to produce characteristic planes, and the force counteracting the attractive forces of the molecules, namely, surface tension. The ultimate aim of the first force is to produce normal planes at right angles to the lines of attracting force, while the second tends to produce sphericity. Which of the two forces will predominate depends upon conditions of temperature, fluidity, size of particle, etc.; but evidences of both are very commonly observed in crystals bearing characteristic vicinal faces. Likewise, Goldschmidt has shown that during the formation of an etch cavity there are two opposing forces at work, the one striving for a rounded pit, the other for the development of definite crystal faces, with the result that facets of vicinal character are often produced. However, such faces, in the opinion of the writer, are seldom truly curved, but may often represent a series of individual reflecting surfaces, plane in character, but giving, in their profusion, the effect of a rounded surface.

On this point, McNairn[46] draws the following conclusion: "Evidently then the continuity of the light-paths is not due to the curvature of the figure faces, but to the fusion of reflections from numerous pits." The resultant tendency, then, in the growing etch figure is, in general, the development of approximately plane faces of low reticular density, which are in no way

[45] E. T. Wherry, Pres. Address, M.S.A., Wash., D. C., 1923; Am. Mineralogist, **9**, 1924, p. 50.

This idea was also discussed and illustrated by Prof. C. H. Desch of Sheffield at the 1924 meeting of the British Association for the Advancement of Science, held at Toronto.

[46] *Op. cit.*

anomalous or accidental in their mode of origin. Their likeness to vicinal faces is thus pretty definitely established. This is a fact of considerable importance, when it is remembered that vicinal faces are normally symmetrical in accordance with the symmetry content of the crystal upon which they are developed.

CHAPTER IV

ANOMALOUS ETCHINGS

Anomalous Solution Phenomena.—If the term " anomalous etch figure " is accepted with its original meaning, it may be said that such etchings are those that do not conform to the symmetry qualities of the crystal upon which they appear. It is evident in this connection that figures undergoing the process of maturing are not to be considered as truly anomalous, although a few exceptions have come under the writer's observation. From this it follows that the anomalous character may be due to development within the etching itself or merely to the position and orientation of the figure upon the face of the crystal. Furthermore, through unrestricted development, the anomaly may become so accentuated as to give rise to solution canals or channels, often following definite directions. These, however, may more correctly be termed " solution phenomena," as their relation to cleavage is often very evident. The so-called " schlauchförmigen Fortsätze " (pouch-shaped processes) of Vater, and the " schnabelförmigen Kanäle " (beak-shaped canals) of Baumhauer, in view of their connection with mature pits, do not permit of such ready explanation, and are consequently truly anomalous. The beak-shaped protuberances which grow out from the etch pits usually tend to lower the symmetry and often reduce a symmetrical etching to one without symmetry planes.

Such forms as these are not uncommonly observed on both artificially and naturally etched crystals, and to one employing the etch method their appearance is always of great interest. Various investigators have made brief mention of these anomalous growths and divers opinions have been expressed in attempts to explain them.

Dr. Wherry [1] is inclined to attach considerable importance to certain types of anomalous figures which are the result of momentary solution, and which in his opinion represent the surface symmetry of the crystal. If this be the case, one would expect greater uniformity in their development, when produced under uniform conditions, than actually results. For instance, the (100) form of apophyllite may or may not show these anomalous immature pits. Certain portions of a given crystal face may develop these asymmetric pits in the incipient stages of solution, while other portions of the same face, acted upon by the same solvent at the same time, may show no trace of them. Instead, exceedingly small diamond-shaped cavities may form, which to all appearances are identical with the symmetrical mature etchings. If these immature solution cavities reflect the molecular configuration at the surface of the crystal, one would not expect such variation in grade of symmetry. It may be possible also that submicroscopic irregularities of the crystal surface influence the shape of these pits during the earliest stages of solution, and that they gradually assume a definite form as the solution becomes more and more constrained in accordance with the crystalline forces. Thus it appears that no fully acceptable explanation is at present available. Whether or not either of the suggestions mentioned above has any bearing on the ultimate solution can only be discovered by further study of these interesting solution phenomena, various forms of which are discussed in the pages following.

Haushofer [2] called attention to the appearance of etch figures which, because of beaked and tube-shaped growths, did not conform to expected symmetry. Baumhauer,[3] in 1870, observed, on the base of calcite, etchings of two kinds which did not agree in symmetry; these exceptional forms he concluded were anomalous. Becke [4] likewise observed anomalous, mono-

[1] Personal communication.

[2] Ueber den Asterismus und die Brewsterwschen Lichtfiguren am Calcit, u.s.w, München, 1865.

[3] Pogg. Ann., 140, 271; also Z. Kryst., **30**, 1899, p. 97.

[4] Min. petr. Mitth., **11**, 349.

symmetric etchings on the octahedral face of certain fluorite crystals. Tschermak,[5] in his studies of the rhombohedral carbonates, encountered asymmetric etchings on the rhombohedron face of magnesite and siderite. Concerning siderite, Baumhauer [6] has also called attention to exceptionally beautiful anomalous etchings, as follows: "Besonders schön sind die schlauchförmigen Fortsätze am Siderit," and has further shown that the dissymmetrical character of the etchings is directly attributable to beak-shaped canals extending into the interior of the crystal.

Beckenkamp [7] in his studies of the symmetry of crystals, especially of barite and aragonite, has described in some detail anomalous etchings of enantiopolar character. Thin plates were found to contain pits, which on either side were oppositely directed, and which could not well be explained by means of twinning or surface irregularity. (Similar anomalies had also been noted by Becke, on cleavage plates of fluorite.) In not a few cases, symmetrical figures modified by conical hollow points extending outward into the interior of the crystal were observed on (010) of aragonite. These processes were often attached to one of the outer corners, or arose from the interior deeper portion of the pit.

The so-called etchings of diopside and augite, described as anomalous by Pelikan,[8] and previously alluded to in this book, were later shown by Baumhauer [9] to permit readily of a different explanation. The former author suggested a direct relationship between the exceptional form of the etch figure and the chemical constitution of the variety of pyroxene, but the explanation offered by the latter is far more plausible, when it is remembered that transitional etchings are often very different in shape and orientation from the mature pit.

Beckenkamp [10] likewise observed anomalous figures during

[5] Min. petr. Mitth., **4**, 121.
[6] Z. Kryst., **30**, 1899, p. 99.
[7] Z. Min. (**14**, 375), (**17**, 321), (**19**, 241), (**27**, 538), (**28**, 69).
[8] Min. petr. Mitth., **16**, 16.
[9] Z. Kryst., **30**, 1899, p. 101.
[10] Z. Kryst., **28**, 1897, p. 87.

his investigation of barite. The faces (102), (001), (110) were commonly marked with hooked and tube-shaped projections of various kinds, which through transition materially altered the shape of the etchings. Their origin was not restricted to the deeper portion of the pits, but sometimes occurred in the very outermost part. Continued solution seems to have resulted in accentuation of the anomalies, a study of which brought Beckenkamp to the conclusion that the solution of the crystal, and likewise its growth, stand in causal relationship to the electrical polarity of the molecule.

Further data on anomalous etchings are afforded by Baumhauer,[11] through his investigations of colemanite, the (010) form of which revealed peculiar " schlauchartigen Fortsätze " extending from the etch pits into the interior of the crystal. The manner of attachment and direction of these beaks was not uniform, but was observed to vary with the figures. Occasionally, dark, pointed processes were observed on (100) and (001) but his observations were not sufficiently numerous to enable him to establish any definite relation between the anomalous etchings of (010) and those of the latter two forms.

Koller,[12] during an extensive investigation of the Binnenthal dolomite, called attention to beautiful anomalous etchings (schlauchförmige Kanäle) developed on the rhombohedron through the action of acetic acid. The beaks extended out uniformly from the central portion of one side of a quadrilateral pit, and appeared in striking contrast to the etchings produced by other solvents.

McNairn,[13] in a study of etch-figure growth, discussed at some length these anomalous forms. According to his observations, three general types of beaks are commonly observed during etching processes, namely, the crack beak, normal beak, and tubular beak. In the writer's experience it would seem that these terms adequately cover most of the solution beaks, although occasional forms are encountered which render classification

[11] Z. Kryst., **30**, 1899, p. 102.
[12] Neues Jahrb. Min. Geol. Beil. Bd., **42**, 1918–19, p. 496.
[13] *Loc. cit.*

difficult, as it is possible for transitional beaks to develop. A " normal " beak, on the base of apophyllite, through continued solution became one of tubular character. However, between the two varieties, " normal " and " crack " beaks, there is apparently a distinct difference. As pointed out by McNairn, there seems to be a relation between the direction of maximum solubility and the development of the " crack " beak. This fact was also observed by the writer, some years ago, during his study of the rhombohedral carbonate etchings, and attention was called to these " modifications " or " appendages " in a paper [14] embodying the results of the investigation, published some time later. Similar beaks were observed by the author [15] on (120) of topaz when etched with potassium hydroxide fusion; as noted in the case of calcite, these are continuous with the axis of elongation of the figure. However, if the chemical character of the solvent is materially changed, the direction of greatest solubility may also change, but it does not follow that beaks will again appear continuous with this new direction of easy solubility. It is true that the etchings produced on the $(11\bar{2}0)$ prism of Cumberland calcite by nitric acid and hydrochloric acid revealed beaks, but they were much less common in the case of the former acid, and, when cold citric acid was employed, not only did the direction of elongation of the etching change, but the beaks entirely disappeared.

In a recent investigation of some of the doubtful symmetries, the author noticed some rather unusual beak development, particularly in connection with the etching of apophyllite. As before mentioned, two kinds of figures may be developed on the (100) form of this mineral through the action of very dilute H_2F_2. The one type experiences very little change in outline or internal arrangement of faces during the process of maturing; the other type of figure passes from a very irregular, shallow, shapeless cavity to a definite diamond-shaped pit. With the latter no beaks were observed, but in the former type of etching " normal " beaks were often numerous. The conditions under

[14] Am. J. Sci., **45**, 1918, pp. 210 and 213.

[15] The Etching Figures of Topaz, Am. Mineralogist, **6**, p. 73, 1921.

which the beaks appeared may well be considered here, as follows:

A colorless, transparent crystal from Paterson was immersed in very dilute, cold H_2F_2 (approx. $\frac{1}{2}$ cc. H_2F_2 to $9\frac{1}{2}$ cc. H_2O). At the end of fifteen minutes the prism (100) was covered with minute diamond-shaped pits, well scattered, and showing a decided tendency to arrange themselves in rows parallel to the basal cleavage; but no figures of type 2 were present. At the end of one-half hour the crystal was excessively channeled parallel to basal cleavage, with some normal development of the etch figures. After an hour's immersion, the acid had eaten its way into the crystal between cleavage lamellæ to such an extent that the crystal fell to pieces even with cautious handling. (Such excessive lamination is not common in H_2F_2.) At this stage a few anomalous growths appeared, a drawing of which may be seen on Plate I, Fig. 12, p. 61. These beaks are beautifully developed, reaching out into the interior of the crystal, from the deeper portion of the pit, and are usually of uniform direction, normal to long axis of the figure. It should be noted, however, that occasionally rights and lefts appear on the same face. In one particular instance this relation was most striking, especially since optical examination gave no evidence of twinning. Through continued immersion this anomaly becomes accentuated both in number and character. At the end of two and one-half hours the irregular shapeless cavities of type 2 began to appear, and gradually took definite form. (In connection with a statement previously made by the author concerning the influence of the physical character of the crystal face upon the etching, it may be well to add, at this point, that a small, more perfect, transparent crystal of apophyllite was subjected to the same treatment, under identical conditions, as the larger crystal described above; and at the end of twenty-five minutes one prism face of (100) revealed not a single etching, while the other faces of this form bore a few small pits confined to the more uneven portions of the face.)

The (100) form on apophyllite, when treated in a potassium hydroxide fusion, reveals but few beaks, and these are tubular

in shape, occasionally attached at either end to an oval etching. Their general direction is that normal to the C axis, and, like those of the base, they suggest a relation to the cleavage. These tubular beaks are thus often comparable to the solution channels found on the surface of crystals. Very similar figures of natural origin were observed on a beautiful transparent crystal of Paterson apophyllite, but no beaks could be found. The striking similarity of the natural and artificial etchings is suggestive of a natural alkaline solvent which is wholly in harmony with zeolite origin.

The base of apophyllite, under usual conditions of etching, may show solution channels, some of which prove to be very exceptional, as may be seen from Photo. 8. The spindle or cigar-shaped forms, with very few exceptions, strike 45° to the basal edges and may suggest secondary lines of weakness, and, furthermore, tetragonal symmetry.[16] In view of this, such forms are not truly anomalous, as previously stated by the writer, although the specific shape which they assume is not readily explainable. Why solution proceeds so vigorously in a definite direction from a given point, gradually widening the channel as it continues, to end abruptly as a tapering extremity, is not easily explained. Normal solution channels do not vary in width, as a usual thing, and are often indicated by definite rows of etch figures; but such is not the case with the forms just mentioned. They were produced on a Paterson crystal of exceptional transparency and regularity of surface, through one-half hour's immersion in very dilute H_2F_2 (strength 5 drops acid to 20 cc. H_2O), and only the one crystal, among dozens etched, revealed this peculiarity of solution on the basal face.

Natural etch figures were found to be numerous on the base

[16] F. M. Jaeger, in "Principle of Symmetry," p. 179, makes the following statement: "The apparently tetragonal crystals of potassium-ferrocyanide, of strychnine-sulphate, etc., and of minerals like idocrase, apophyllite, etc., are beyond all doubt optically biaxial." On p. 189, while speaking of the results of X-ray examination, he continues: "We observed in the case of apophyllite, potassium-ferrocyanide, benzil, benitoite . . . that, even from apparently homogeneous and faultless plates, patterns of a lower symmetry were obtained than should be the case with respect to their proper symmetry."

of two or three Paterson crystals, and in each case the square pyramidal cavities were modified by thread-shaped solution tubes, indicated in the photograph by dark shadows reaching out from the bottom of the pits far into the interior of the crystal. These often attained a length many times the diameter of the etch figure, as is evidenced through change of focus following them to their extremities, and in very few cases were they observed to follow a direction normal to the base; they very soon turned outward in various directions, describing a flat arc. (See Photos 13, 14.) Artificial etching of this face occasionally revealed beautiful tubular beaks drooping into the crystal parallel to the *C* axis for perceptible distances, but nothing similar to those of the natural etchings was observed. It should be remembered, however, that natural etch figures occurring on a crystal face, regardless of their matchless perfection, may occasionally show great variation in shape and orientation, in a manner not explainable through transition, owing to the fact that the crystal may at different times in its life history have been subjected to repeated etching processes by solvents of variable chemical constituency, each solution leaving upon the crystal a record peculiar to itself. Just as habit is usually uniform for a given locality, so it might be expected that conditions of etching would likewise remain fairly constant over smaller areas; but the etch figure is rather a delicate indicator of the chemical variation of the solutions instrumental in its growth, with the result that crystals of the same habit in a given locality may reveal different etchings. This has been noted by Sommerfeldt [17] on barite, where two distinct periods of etching were recorded on the same crystal, producing compound etchings conformable with lower than holohedral symmetry. Such growths, he concluded, were anomalous.

The (111) form, like others of apophyllite, revealed a few very definite beaks, extending from the side of the pit, modifying the monosymmetrical etching in a manner very similar to those of the prism face. (See Photos. 3 and 7.) When focusing on the crystal surface, these normal beaks are usually indicated by dark

[17] Centr. Min. Geol., 1902, 97–103.

shadows, which, if investigated through downward movement of the microscope tube, are found to be definite hook-shaped cavities leading out from the etch cavity; they may be entirely invisible in reflected light. Indeed, the so-called beaks are of peculiar interest. Why they develop on certain etch figures, and not on others of the same face; why on certain faces they assume a like orientation; why they form as a result of special conditions, and so commonly in such peculiarly hooked cavities; and finally, why they should be so universally encountered in the etching processes, are questions which must be answered in any attempt to explain them. As previously stated, different opinions have been advanced respecting the forces controlling their origin.

It has been said that anomalous etchings are those which do not wholly conform with expected symmetry, and which often permit of variation of interpretation. The etch figure may be considered anomalous by its orientation only, or through peculiar development within itself. Anomalies of the first kind usually arise through twinning, which may be indicated by like orientation of the figures over a certain area of the crystal face, with a reflective orientation in an adjacent area. At the twin contact, two asymmetrical figures may be so joined as to result in a symmetrical form. A few illustrations may serve to clarify this point. In the case of polysynthetic twinning in albite, as shown by Walker,[18] the monosymmetric figures of compound nature apparently conform to monoclinic symmetry, but, when developed between the twin contacts, they result in asymmetric etchings conformable with the true symmetry. A similar increase of symmetry has likewise been observed on the etchings of the second-order hexagonal prism of tourmaline, but in this case it was the result of striations. Similarly, symmetrical figures may give an appearance of lower symmetry if developed on faces that are excessively striated. Anomalous etchings derived from twinning led Gaubert [19] to the conclusion that dolomite was of rhombohedral hemihedrism as are the other rhombohedral

[18] Am. J. Sci., 5, 1898, p. 183.

[19] Neues Jahrb. Min. Geol. Beil. Bd., Vol., 1918-19, p. 493.

carbonates, a view greatly at variance with the results of Koller [20] and also with those of the writer. The former, by means of etchings, has pointed out that dolomite from Binnenthal often shows intricate twinning, and that the monosymmetrical figures of Gaubert probably had their origin in this cause. The same fact was pointed out by Baumhauer [21] many years ago, in connection with both dolomite and nepheline, and photographs were reproduced which beautifully illustrated the very irregular boundaries of the twinned individuals. Earlier works by the same author, on quartz, show that it is possible by means of etching to identify most complexly twinned enantiomorphous forms. Beckenkamp [22] states that many crystals that usually appear holohedral may through etching be observed to represent the union of plus and minus forms. The investigation of barite and aragonite by the same author [22] has given rise to some rather unusual anomalous etchings of enantiopolar character, developed on their basal plates. These figures, which occupied reversed positions on the opposite sides of the plates, are apparently not dependent upon any foreign admixture or extraneous bodies, but upon inherent properties within the molecule, as Beckenkamp states that the polar appearances were most characteristic on perfectly clear crystals, and also that the polarity of the barite molecule is not a mere transitory property, which appears through heating and cooling processes, but a lasting phenomenon not often observed on holohedral crystals. He was able to show that the enantiopolarity of the etch figures of barite corresponded to the pyro-electrical content of the crystal. However, centrosymmetric symmetry does not yield pyro-electricity, hence the only conclusion seemingly available is that of twinning. Since this is often supplementary in nature, the resultant heterogeneous character may not always be optically visible, but, through etch figures, by pyro-electricity, or by magnetic investigation, the pseudo-symmetrical crystals may be found to consist of aggregates.

[20] Neues Jahrb. Min. Geol. Beil. Bd., Vol., 1918–19, p. 488.
[21] *Loc. cit.*
[22] Z. Kryst., **28**, 1897, p. 91.

A very extended study of the anomalous character of many of the etchings of the aragonite group has led Beckenkamp[23] to some important conclusions, namely, that normal etchings are dependent upon the molecular arrangement, while the anomalous figures are attributable to the electrical charges of the molecule. Conclusions of very similar nature were reached by Westhoff and Viola from their studies of the anomalous figures of aragonite, and likewise Sommerfeldt, in connection with some natural etchings of barite, all of which seem to indicate that the electrical charges of the molecule exert an important influence on the development of certain etch figures, and further Beckenkamp concludes that barite and aragonite crystals represent a complex of eight symmetrically oriented parts or individuals, the strength of his convictions concerning which may be gained from his own words as follows: "dasz ein allseitig ausgebildeter Aragonit- oder Baryt-krystall einen Complex aus acht Individuen darstellt, ist nicht Hypothese, sondern unmittelbare Beobachtung." To illustrate further the connection between anomalous figures and crystal symmetry, the observations of Beckenkamp may again be cited. He concludes that the aragonite group is not orthorhombic holohedral, and, concerning aragonite and barite in particular, he remarks[24] "Dasz ein rings angebildeter Aragonit oder Barytkrystal einen zwillingsartigen Complex aus mehreren Teilen darstellt, ist somit durch alle nur irgend möglichen Beobachtungsmethoden unzweifelhaft festgelegt." However, recent x-ray data appear to indicate holohedral orthorhombic symmetry for barite. Also as may be seen in a later chapter of this book, there is no evidence of complex grouping shown by the etchings of this mineral which would lead one to suspect that it is hemihedral.

The explanation concerning the beaks frequently observed on etchings is not so easily arrived at. H. Vater[25] suggests that the tube or pocket-shaped processes of many anomalous etch figures may be explained on the supposition that in certain parts

[23] Z. Kryst., 44, 1908, p. 358.
[24] Z. Kryst., **44**, 1908, p. 359.
[25] Z. Kryst., **32**, 1900, pp. 34–36.

of the crystal, where the included foreign material had been concentrated, the anomaly has been developed through the process of etching at this point, causing an irregular cavity to be dissolved out. Westhoff [25] expresses a similar view concerning the shape and position of anomalous etchings. Such a process is possible, as it is well known that inclusions of foreign material affect solution, and indeed zoning or banding of laminæ of special chemical constitution may, through heating, set up differential stresses within the crystal, which may operate to cause distortion of the figures. It is certain, however, that not all anomalous etchings of this peculiar nature can be accounted for in this way; in fact, this theory does not explain the beaked shape, or does it take into account the fact that very often the beak is developed only on one side of a large number of etchings occurring on a crystal face. The above explanation can hardly be applied to a single occurrence of the so-called "crack" beaks; and furthermore, the writer fails to see why there should be any uniformity of shape at all, if heterogeneous admixture be the cause. On this point Beckenkamp [26] states as follows: "I have already (1889) remarked the possibility that foreign admixtures may change the physical and chemical behavior of a crystalline substance. But the manner in which Westhoff represents this agency is theoretically impossible and contrary to observation." Apparently, then, the assumption, that included foreign material causes the beaks, must be dismissed as untrustworthy and improbable.

A much more direct and probable explanation is set forth by McNairn,[27] although here again certain features become rather speculative and not in all cases according to the observations of the writer. However, this explanation does have the advantage of being applicable to pure chemical substances as well as those containing much impurity. It is suggested that the "crack" beaks, in view of their relation to the longer sides of the etchings, represent directions of more rapid solution, an observation in harmony with that made by the author during the etching of the

[26] *Loc. cit.*
[27] *Loc. cit.*

second-order prism of calcite, upon which the crack beak is beautifully developed. In describing these anomalous forms the author [28] says: "While the figures are simple they are unique in that any one of the four faces may be extended as a groove at the acute angle, and appears as an appendage curved toward the figure and varying in length with the stage of development. Very often a figure contains two, one at each acute angle. The general direction of these modifications is always parallel to the prism edge." In reviewing this slide the writer was in no case able to find a beak attached to the obtuse angle of the rhombic figure, and further observed that in every case the extension could be traced either to the direction of maximum solubility or to traces of cleavage. There is also some suggestion, in the arrangement of the beak with respect to the figure itself, which would lead one to expect a later facial development adjacent to the beaks; and the idea that the development of beaks is in some cases a step in the process of maturing will be gained from the discussion which follows.

On the (120) form of topaz [29] the crack beaks, as developed by potassium hydroxide fusion, reveal this relation even more strikingly. Not only do they appear as a continuation of the longer contour of the pit, but they are invariably attached to the same etch face of all figures and turned in the same direction over the entire face. More than this, their directions on adjacent (120) faces are reversed to meet the symmetry requirement of the type. Their truly anomalous character lies in the unequal development often observed at either end of the figure. However, an important point to be noted here, with which the writer wishes to supplement the suggestion of McNairn, is the apparent transition of the beaks into normal and symmetrically placed etch faces of very high intercept, observable only in the mature etchings. The curvature of the beak, then, being always directed toward the shorter side of the figure adjacent to which there is subsequent development of very flat faces, points to the beak as being dependent upon two forces, one dominating

[28] Am. J. Sci., **45**, 1918, p. 210.
[29] Honess, *loc. cit.*, p. 73.

force causing solution parallel to the elongation, and another secondary force acting transverse to this in the direction of the figure; the two taken together form a curved projection, which may eventually become a part of the figure proper through facial development over the partially enclosed area, as seen in Fig. 5, AA'. This transition may be illustrated according to the drawings:

Fig. 5.

The faces AA', being last to develop with very indistinct contour, and having a position so near to that of the prism face itself, may very easily be missed in one's analysis of the figure. Thus the anomaly entirely disappears, resulting in a monosymmetrical etching, and the crack beak so well developed in the primitive form is only the forerunner of a face later to develop at that end of the figure. In the case of topaz, just cited, the beak appears early in the etching process and is subsequently rendered less conspicuous through development of the figure faces; but the fact that the beaks may appear late in the growth of the figure is evidenced by the (011) form of barite when this mineral is boiled in nitric acid. The immature pits possess no beaks; but, as solution continues, etch facets of very steep slope develop at the base of the pit and gradually assume a perpendicular or even overhanging position, which results in the formation of a normal beak at that point. It would be interesting to know if others have made similar observations in connection with so-called beaks. However, this transitional development in no way modifies the previous statement concerning the relation of the beak to the direction of greatest solubility; it only serves to substantiate that statement, and further, by virtue of its connection with the evolution of the figure, points to a causal relationship between molecular structure and this type of beak, a conclusion which is incontestable.

However, further consideration may be of interest here. If,

instead of KOH fusion, a fused mixture of CaF_2 and $KHSO_4$ be employed on (120) of topaz, the development of the end faces keeps pace with that of the facet producing the elongation, in consequence of which there are no crack beaks developed at any stage of the process, and it would seem that chemical control had been instrumental in their elimination, by checking the rapid solution parallel to the figure's elongation and accelerating solution in those directions which result in the growth of the end (*a*) faces and consequently in a balanced figure. However, normal beaks are developed in profusion on the mature etchings. (See Fig. 6.) In a comparison of the figures produced by the two solvents, the author in this connection states,[30] "These figures (produced by CaF_2 plus $KHSO_4$) are very similar to those just described in the mature stage, but in the earlier stages of development the pointed appendages, so prominent on the KOH figures, do not appear to be present." Thus it seems that by chemical variation of the solvent the development of beaks may be accelerated or diminished through corresponding changes in solution directions, that solvent being considered most desirable which creates during the development of the etch pit a solution condition of balance and equilibrium, just as a similar condition during the process of crystallization tends toward the development of a more perfect crystal. A distorted or anomalous etch figure, then, may often be corrected through the use of such solvents as will tend to eliminate the excessive solution producing the beak, or bring other solution forces to prevail in such a manner as to counteract it. According to this view, therefore, a decided change in the chemical nature of the solvent may often

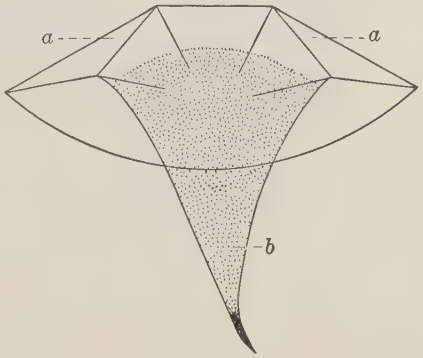


FIG. 6.

[30] Am. Mineralogist, **6**, 1921, p. 73.

eliminate beaks altogether, or give rise to beaks of different nature and point of attachment, a change which has been actually observed by the author during his investigation of calcite, apophyllite, barite, celestite, and other minerals. Beaks were obtained in great profusion on (1120) of Cumberland calcite through the use of 10 per cent hydrochloric acid, but they disappeared entirely with the use of citric acid, their disappearance being accompanied by a radical change in the shape and elongation of the figures. Dilute hydrofluoric acid produces normal beaks on many of the figures developed on (100) of apophyllite, but none are to be seen on the etchings obtained on this mineral through alkali fusion. Further evidence of the soundness of this conclusion is to be observed in the experiments of McNairn, who concluded that HCl of medium strength was more favorable to the development of beaks on colemanite than a weaker acid. Hence, there can be little doubt that the beak is the normal product of special conditions of etchings based upon differential solution and that it is often a source of misinterpretation. This fact at once suggests to the investigator the advisability of using a number of solvents before arriving at a definite conclusion respecting the symmetry of a crystal, as such beak distortions are not to be interpreted as necessarily characteristic of low symmetry any more than are crystals of distorted habit. The view suggested by some, that beaks may possibly be caused by inclusions of molecular grouping possessing lower symmetry than the host, along with other fortuitous causes, at once appears far-fetched and improbable.

The "normal" beaks, or pouched-shaped cavities, being developed from the deeper portions of the pits, often penetrate to a considerable distance the interior of the crystal; but their relation to the etch figure is so evident that some solution process, similar to that mentioned for the "crack" beak, is suggested as accounting for their origin. McNairn [31] favors the view that the beak is formed by the solution resultant of several forces acting together, and that the face having the greatest attraction for the solvent determines the direction which the

[31] Trans. Can. Inst., 11–12, 1916, p. 262.

cavity shall take. If this idea is developed further, it leads us to assume that the consecutive development of a series of more insoluble faces may tend to force the solvent to change its course, resulting in a curved or hooked appearance. Evidence of such a process is found in the fact that beaks may proceed from the side of the figure as well as from the bottom. (See Fig. 12, Plate of Anomalous Etchings p. 61.) Their origin, then, is due to differential solution, and is quite similar to the development of the crack beak, as suggested by the writer. This view is also in perfect harmony with his suggestion, set forth earlier in this book, respecting the attack on the crystal surface by the solvent, and its consequent dislodgment of the molecules governing the distribution of etch figures. That the tubular solution channels are governed more through cleavage direction seems certain from the experiments of the writer, although the tubular beaks previously described on apophyllite assumed a uniform direction generally normal to the basal cleavage; but since this mineral is so exceedingly soluble parallel to its vertical axis, the fact that solution tubules formed in the bottom of the basal pits is not in the least surprising. These, regardless of the fact that they were not curved, were probably more in the nature of normal beaks. These solution canals may often be conceived of as lines within the crystal, along which it has been particularly soluble, and which generally, though not always, represent some definite direction. Etch figures may form at the mouth of these canals where a point of ready attack is at hand. From the nature of some of these canals one wonders if they may not in some way be connected with the elongated cavities of primary origin, often produced in crystals through rapid crystallization. For other canals this explanation would not seem to suffice, so direct is their relation to the corrosion figures of the crystal.

Because of the importance of the so-called anomalous etch figures in their relation to crystal symmetry, and the frequency with which they are encountered, it has seemed fitting to discuss at some length their nature and mode of origin. Although considerable difference of opinion has been expressed by those who have observed these peculiar forms, it has seemed to the

writer that they are not usually the result of admixture, or of any accidental cause, but of normal solution processes incurred through special conditions. This conclusion has been arrived at mainly from a careful study of the anomalies observed on topaz, celestite, calcite, barite, and apophyllite, during the etching of these minerals.

It is believed that there are two distinct types of anomalous etchings. The first type consists of those confined to complex crystals exhibiting other anomalies, such as optical irregularities, and usually associated with intricate twinning. Such anomalous etchings may often prove valuable in the elucidation of complexly intergrown crystals, such as leucite or nepheline. The second type comprises etchings that exhibit beaks of various kinds. These may appear on almost any crystal under favorable conditions, and may suggest a lower symmetry than that actually possessed by the crystal upon which they occur.

Considering the value of photographs and drawings in a treatise of this kind, the writer has carefully selected, from his data and from those of others, several of the more common types of anomalous etchings, drawings of which appear on the plate appended.

KEY TO PLATE I

Anomalous Etchings Showing Solution Tubes

Fig. 1	(010)	Aragonite	(After Beckenkamp)
Figs. 2, 3	(102)	Barite	(After Beckenkamp)
Fig. 4	(001)	Barite	(After Beckenkamp)
Fig. 5	(110)	Barite	(After Beckenkamp)
Fig. 6	$(10\bar{1}1)$	Dolomite	(After Koller)
Fig. 7	(010)	Colemanite	(After Baumhauer)
Fig. 8	(010)	Colemanite	(After Baumhauer)
Fig. 9	(010)	Colemanite	(After McNairn)
Fig. 10	(010)	Colemanite	(After McNairn)
Fig. 11	$(11\bar{2}0)$	Calcite	(By the Author)
Fig. 12	(100)	Apophyllite	(By the Author)
Fig. 13	(111)	Apophyllite	(By the Author)
Fig. 14	(001)	Apophyllite	(By the Author)
Text Fig. 5	(120)	Topaz	(By the Author)

See also Fig. 14 *a–b* (102) Barite; text, Fig. 13 *b* (011) Celestite; and Photo 62 (by the Author).

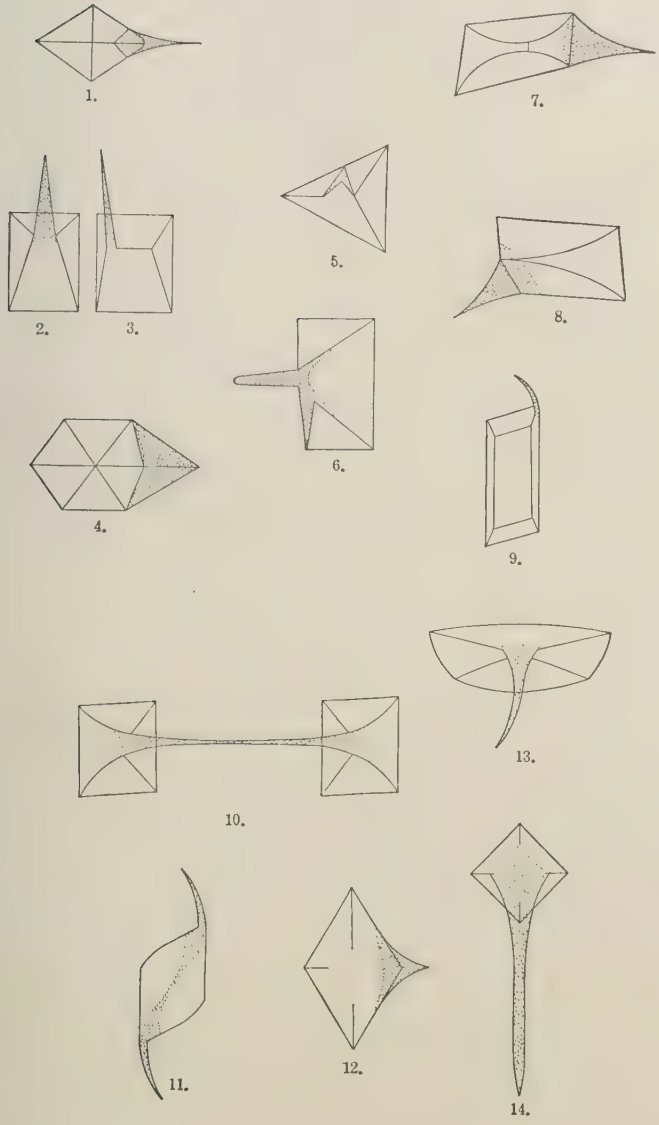


PLATE I.

Anomalous Solution Channels and Cavities Attached to Etch Figures.

CHAPTER V

THE IMPORTANCE OF THE ETCH FIGURE IN ISOMORPHISM

The Etch Figure and Isomorphism.—The investigations of previous years bearing on the value of the etch figure in determining isomorphism have unfortunately not led to harmonious conclusions. The disagreement may be due partly to the lack of a uniform standard by which such results may be judged, and partly to the inability of certain investigators to appreciate fully the sensitiveness of the etch figure to temperature and chemical variation of the solvent employed, and to the time through which the etching continues. These factors must be carefully considered if correct comparisons are to be made, as it will be necessary to select a solvent which will yield good results for all members of the series to be tested. For example, all of the rhombohedral carbonates, except magnesite and siderite, would yield good figures in either HCl or HNO_3 after ten or twenty seconds' immersion, but the carbonates of iron and magnesium would not be appreciably affected in so short a time. As the shape of the figure is a function of its age in many cases, the time through which corrosion proceeds becomes an important factor, and particularly so when the etch figures are not especially simple in their arrangement of faces. Daly [1] in his "Etch Figures of the Amphiboles," emphasizes this fact in the following words: "In many instances it has been exemplified that a systematic comparison of etch figures on different species will be of most service if the observer recognizes the principle that there is a decided change in the etch-pit characteristic of any face, in accordance with the stage it has reached in the

[1] Proc. Am. Acad., Sci., **34**, 1898–99, p. 427.

process of maturing from an initial figure to the often very different figure peculiar to an advanced stage of corrosion." This urgent need of control, then, cannot be overestimated in experiments seeking quantitative data.

Baumhauer [2] investigated the etchings of several isomorphous groups in the hope of learning something definite respecting the similarity of the figures obtained upon the members of a series. Four of the groups are as follows:

1. The iron, chromium, and aluminum-potash alums.
2. The nickel-potassium, nickel-ammonium, and iron-ammonium sulphates.
3. The rhombohedral carbonates of iron, calcium, and magnesium.
4. The members apatite, mimetite, pyromorphite, and vanadinite of the apatite group.

The first group when etched with water revealed very similar etchings, likewise the second group; but the members of the third and fourth series when etched with acids manifested some dissimilarity. The alums showed, on corresponding faces, figures of great similarity both in shape and position; those of the sulfates differed primarily in position. The carbonates, siderite and dolomite, appeared from the position of their etchings on the unit rhombohedron to be distinct from calcite. Later investigation, of course, by Tschermak, Haushofer and Koller, and also the present writer, has shown by means of etch figures that dolomite is tetartohedral in symmetry and consequently not isomorphous with the other rhombohedral carbonates. Von Kobell [3] also in his earlier work called attention to differences in the asterism revealed by dolomite in comparison to calcite, and likewise to an exceptional orientation of HCl etchings on the rhombs of both siderite and magnesite. Tschermak,[4] in view of the many anomalous etchings obtained on the carbonates, evidently did not have pure simple crystals, in consequence of

[2] Resultate, p. 36.

[3] Sitzungsber. Bayr. Akad. Wiss., 1862, Bd. 1, cited by Baumhauer, p. 37.

[4] Min. petr. Mitth., 4, 99.

which the dissimilarity of the figures is not surprising. Later, Tschermak himself agreed with Becke and Baumhauer that the figures of the carbonates, with the exception of dolomite, were undoubtedly monosymmetric and quite similar ("Resultate," p. 68). Still later, Retgers,[5] in a very valuable paper, "Beiträge zur Kenntniss der Isomorphismus," expressed the view that not only must the constituent compounds of an isomorphous series be replaceable in all proportions, and likewise possess a lack of chemical combination such as double salts, but that the etch figures produced on like faces under the same conditions must be similar in shape and of the same symmetry. With this latter criterion in mind he suggested a non-isomorphous relation between calcite on one hand and magnesite and siderite on the other ("Resultate," p. 38), a view later held to be incorrect. In fact, the writer failed to see any justification for such a statement while comparing the etchings of these carbonates.[6] However, it may be mentioned that the atomic volume of Ca is quite different from that of Mn, Mg, or Fe; a fact which may explain the inability of $CaCO_3$ to mix readily in all proportions with the other molecules of the isomorphous carbonate group, which among themselves are freely miscible. There is a suggestion of similarity between the relation of the calcium, magnesium, and iron carbonates and the relation of the sodium to potassium and ammonium in the chlorides; but the two cases are hardly comparable, for the difference in the position of the etchings is one indicating lower symmetry in the case of potassium and ammonium, more in the nature of dolomite when compared to the other rhombohedral carbonates. This would seem to show that etch figures are of some value in determining isomorphous relationships, and, should it eventually be proven that ammonium chloride and potassium chloride are, like the sodium salt, holohedral, there would still be the anomalously placed etchings to show that these salts are not truly isomorphous (Krickmeyer, *loc cit.*). To illustrate further his suggestion that similarity of etchings is a necessary criterion in studies of iso-

[5] Retgers, Z. phys. Chem., 1895, Bd. XVI, p. 36.
[6] *Loc. cit.*, p. 201.

morphism, Retgers cites other interesting cases, including the results of Baumhauer [7] on the apatite group. When etched with dilute HNO_3, the base and unit prism of apatite, as well as the unit prism of pyromorphite and mimetite, revealed distinct hemihedral etch figures; but on the base of pyromorphite and mimetite the figures were apparently holohedral. That Baumhauer was not convinced of their holohedral character, however, is evidenced in his later remarks concerning further investigation, which seems to have resulted in establishing undoubted hemihedral symmetry for these doubtful species, including vanadinite. In this connection the writer may add that an isomorphous 1 : 1 mixture of mimetite and vanadinite, known as endlichite, upon investigation was found to yield beautiful hemihedral etchings on the prism face, a fact which tends to strengthen Baumhauer's conclusion. The etchings of this mineral are more fully described in subsequent pages of this book; but incidentally it may be stated that the endlichite and apatite (1010) figures produced by 10 per cent HNO_3 and by hot conc. citric acid are in each case quite similar, while the etchings formed on endlichite by 15 per cent cold HNO_3 acting for twenty-five seconds are comparable to none. Thus, even though there is considerable uniformity of outline among the etchings of this group, necessitated by the fact of equivalent symmetry throughout, there are certain departures from uniformity which must not be overlooked, as is attested by Baumhauer's remark ("Resultate," p. 37) in reference to the fourth or apatite group, ". . . diejenigen der dritten und vierten Reihe beim Aetzen mit Säuren mehr oder weniger bedeutende Abweichungen unter einander aufweisen." But the earlier work of Baumhauer upon the apatite group seems to have stirred Arzruni [8] to deny any quantitative relationship between isomorphism and the shape of the etch figure, on the ground that difference of property of the components of isomorphous bodies leads to unlike solubility toward one and the same solvent, with dissimilar results as a likely consequence. However, through further investigation by Baumhauer, the criticisms

[7] Resultate, p. 39.

[8] Phys. Chemie der Krystalle, 1893, p. 162; also, Resultate, p. 40.

of Arzruni seem to have been met, and the latter in a personal note addressed Baumhauer as follows: "Die Anwendbarkeit der Aetzmethode zu Beurtheilung des Isomorphismus in der von Ihnen erläuterten Form muss ich zugeben." (The adaptability of the etch method to the discernment of isomorphism is admitted.[9])

Further evidence of this relationship is found in the experiments of Baumhauer[10] on the double sulfates, namely, the hydrous sulfate of magnesium and ammonium, and the hydrous sulfate of iron and potassium, as well as on mixed crystals of these molecules. The results again appear to point in favor of Retgers' view, as these substances reveal no essential differences in the form of their etch figures.

The alums,[11] of which brief mention has been made, comprise still another group whose etchings bear great similarity. In the potash alum the pit of the triangular etchings of the octahedron is often truncated by a face lying parallel to the etched face, but the deeper edges rarely possess such modifications. However, a small face lying in the zone $(111)-(001)$ may extend obliquely toward the periphery of the figure. The asterism of such a figure is revealed as a three-rayed star, whose beams are turned to the deepened edges of the etching. On the thallium alum appear also triangular figures, usually without truncations; but, if the octahedral etch facet appears, there are usually other truncations similar to those of potash alum. In reflected light the figures yield a six-rayed star, three beams of which are bright and three less so. Mixed crystals of unlike composition show very similar figures having the properties of either or both of the pure end members of the series.

As a further test of the theory of Retgers, Baumhauer continued his researches through an investigation of the phosphate-arsenate series, comprising hydrogen-potassium phosphate, hydrogen-ammonium phosphate, hydrogen-potassium arsenate, and hydrogen-ammonium arsenate. These tetragonal salts are

[9] Resultate, p. 40.
[10] Resultate, p. 46.
[11] Resultate, p. 45.

of simple prismatic-pyramid habit and when etched with water yield results described as follows:

The etchings on the prism faces of the potassium phosphate and potassium arsenate were almost identical in shape and position, and the symmetry was clearly shown as hemihedral-sphenoidal, or alternating hemihedral. On the pyramid the figures of the potassium phosphate were triangular and composed of three unlike etch facets which by their arrangement corresponded to right and left on adjacent faces at either termination of the crystal, but which became reflective across the equatorial zone after revolution of 90° about the vertical axis The sphenoidal hemihedrism was thus clearly shown on the potassium phosphate, but the symmetry was much more definitely illustrated by the pyramid etchings of the ammonium phosphate. However, between the two there was great similarity. In the case of the pyramidal figures of the potash phosphate, as compared with similar etchings of the potash arsenate, the former salt revealed the hemihedrism more distinctly. The pyramid etchings of the ammonium arsenate, because of surface irregularities, could not be definitely studied. However, while the potash salts revealed sphenoidal hemihedrism, the ammonium salts, when their prisms bore definite etchings, were not similar to those of the former salt, and seemed to point to a lower symmetry. The fact that they required different etching conditions would suggest some molecular difference in their make-up; this was further evidenced by the fact that while the pyramidal etchings of both salt groups were *similar*, the etchings of the prism were *dissimilar*. The ammonium salts possessed etchings on their prism which varied in shape and position, and since in many cases they could not be turned into congruence in the plane of a prism after a revolution of 180° about C, there was in their shape and position a suggestion of lower than hemihedral sphenoidal symmetry. Moreover, their positions on the same face were often anomalous, as if the crystals were twinned on the base. This would suggest another illustration of the fact that a crystal of low symmetry strives for the more perfect mechanical stability of high-symmetry forms.

Thus, in Baumhauer's investigation of this series, even if he has not proven interrupted isomorphism between the potash and ammonium salts, there is something about the results which should stimulate further study of the series, especially of the ammonium members. This demand has been partly fulfilled by Krickmeyer [12] in a study of the isomorphism of alkali salts. His results on potash and ammonium phosphates, which emphasize his inability to obtain unbroken series or to produce mixed crystals with preponderating potash content, even when employing neutral potash and ammonium tartrates, would seem to suggest that Baumhauer's skepticism had been duly justified. It would seem that again the etch figure has yielded helpful assistance in calling to attention the distinctive features of the ammonium salts in a comparison of these with the other members of the series.

Baumhauer [13] in his investigation of the etch figures of the isomorphous rhombohedral hyposulfates of calcium and of strontium, remarked a striking likeness in their corrosion pits. The base and the plus and minus rhombohedrons when etched with water showed the following forms: On the base the etchings were at first triangular with each corner, truncated by a small minus R face. As solution continued the minus R faces approached in size those of the plus R, giving six-sided pits, which on simple crystals were turned with respect to those of the opposite basal face. When, however, the crystals were twinned on the base, the etchings of both basal faces occupied the same position. By means of etching, either a simple or a complex crystal might be recognized with ease. The etchings of the rhombohedron were isosceles triangular pits bounded by three faces, one of the rhombohedral and two of the scalenohedral zones with the elongation parallel to $\pm R/C$. Between the plus and minus rhombohedron faces, Baumhauer could see very little difference.

With the strontium salt the basal figures were less decidedly

[12] Z. phys. Chem., 1896, 21, 53; also Z. Kryst., **30**, 1899, p. 636 (Abstr. Muthmann).

[13] Z. Kryst., **1**, 1877, p. 54.

rhombohedral in character, but similar; while on the plus and minus rhombohedrons of this salt the etchings were entirely similar to those on the corresponding faces of a calcium hyposulfate, a fact pointing further to the position of the etch figure in its relation to isomorphous substances.

The investigations of Wulff [14] on the isomorphous nitrates of lead, strontium, and barium also have a distinct bearing on this question of isomorphism as it is related to etch figures. The corrosion figures of these three salts, as remarked by Wulff, are triangular but turned asymmetrically to the position of that shown by the alum etchings, which indicates a lower symmetry. Furthermore, their positions on tetrahedral faces of opposite sign is opposing, fixing the symmetry of the group as tetartohedral polar. On a right-handed crystal of the lead salt, the etchings of the positive tetrahedral faces are turned to the left (anti-clock wise), and on the faces of the negative form opposite, the figures assume a corresponding position to the right, a condition likewise observed on the salts of barium and strontium, revealing alike similar etchings similarly placed, and a tetartohedral polar symmetry for the group.

Finally, attention should again be called to the very important paper by R. A. Daly,[15] concerning isomorphism among the members of the amphibole group. A series of etching experiments, performed under very special conditions upon the chief members of this group, constitute a vivid illustration of the possibilities of the etch figure in mineralogical research. The results of the investigation are particularly impressive because of the great care exercised by Professor Daly in his selection of material and the extreme caution used in regard to the chemical control of etching conditions, not to mention the minute detail with which the comparative results are described.

For the purpose of a comparative study the prismatic cleavage face was selected and etched under similar conditions, in order to determine, if possible, whether there was any variation of

[14] Z. Kryst., **4**, 1880, p. 142.

[15] A comparative study of etch figures: The Amphiboles and Pyroxenes, Proc. Am. Acad. Arts Sci., **34**, 1898–99, p. 373.

resistance to chemical corrosion among the members of the group; what variation in shape of the etchings, if any, might be observed with change in chemical constitution; and whether the etch figures could throw any further light upon the chemical relations of the species forming this group. Consequently, whether or not the results obtained favor Retgers' view, they have a direct bearing upon this question of isomorphism as evidenced in similarity of etch patterns. In view of the ready accessibility of this paper, only a few of the more important conclusions arrived at by Professor Daly will be here given, namely:

"(*a*) That the manner in which a given face of a crystal reacts to a solvent is influenced to some extent by its physical state.

(*b*) That the shape of an etch figure may change during the process of maturing.

(*c*) That quantitative use of the etch method may lead to results of equal importance with those of other less convenient methods.

(*d*) That on a basis of etch figures the amphiboles may be divided into two isomorphous mineral groups not isomorphous with each other, and all holohedral.

(*e*) That aluminous and non-aluminous varieties may be detected by their etchings.

(*f*) That glaucophane and gastaldite are the same species, and that both may form isomorphous mixtures with hornblende, while arfvedsonite appears to be more or less distinct among the amphiboles.

(*g*) That a hornblende, known as the Philipstad variety, appeared to be so individual in its etchings as to warrant classification as a new variety.

(*h*) That tremolite, actinolite, richterite, and astochite, from various localities and of various chemical composition, yielded similar etch figures on (110); and, where other faces such as (010), (100) and ($\bar{1}01$) were present, a similar likeness was observed."

The author, while etching the sulfates anglesite, barite, and celestite with hot dilute HNO_3, became interested in certain comparisons which suggested themselves when the drawings were considered. The solubilities of these species are so different that the time through which etching continued was not uniform, barite requiring very much longer immersion. A comparative study of the etchings of these minerals may be had from the drawings (Figs. 13, 14, 15). The prism etchings of barite and anglesite are very similar both in outline and orientation. The celestite prism figures are narrower and more elongated and possess a reversed position with respect to those of the other two sulfates. The macrodome and brachydome etchings are very unlike on both celestite and anglesite, while on barite the figures of the corresponding domes are similar, but reversed, so that no comparison can be made throughout the series of corresponding dome faces. However, the figures on the macrodome of anglesite are analogous to those of the corresponding face of barite, but simpler in arrangement of faces. The etchings of the macrodome of celestite are comparable to none. The best developed face of the sulfates of lead and strontium is the (011) dome, but it is noteworthy that the etchings of each in the mature stage are distinctly different. During the etching of anglesite there was noted on this form a very interesting transitional growth of the figures, which may readily be likened to that of the HCl figures on the same form of celestite, and at certain stages in the development the figures of the two sulfates were quite similar. It may be seen from the drawings, however, that the mature forms are unlike. By changing the solvent from HNO_3 to HCl there is a very noticeable shortening of the figures on (011) on both species. The base was not sufficiently developed to permit of satisfactory etching; hence, no comparison was made. It would seem, then, that these minerals show similar etchings when a comparison is made of their prism faces, but such similarity is not constant for other forms, although it must be admitted that conditions of etching cannot be so strictly controlled where there is such a decided difference in solubility manifested by the different members of the group, when immersed in nitric acid.

In the case of calcite and rhodochrosite rhombs etched by hydrofluoric acid, the author was not able to see any similarity. The calcite revealed beautiful elliptical or fan-shaped etchings, not at all similar to the elongated triangular pits of the manganese carbonate. Yet, when these minerals are treated with HCl, their etchings are very much alike.

The facts stated on the foregoing pages summarize repeated attempts to establish some definite statement regarding the association of similarity of etchings with isomorphous substances. It is true that in some cases the relation seems to hold; but it is impossible to determine how widely the shape of the figures may vary and still satisfy the requirements of Retgers' suggestion. Until a more definite meaning can be given to the term "similar," there will always be a variable standard which amounts to nothing more than a series of estimations by various investigators of what may be considered a fitting similarity. It is readily recognized that the etchings of like crystallographic planes of isomorphous substances must be similar to the extent that all must possess the same degree of symmetry; but to expect that the differences displayed by the etchings of a number of corresponding planes which are differently constituted chemically, shall be negligible, would seem not to be in accordance with the theory of solution, as revealed through development of etchings, especially should this similarity be more difficult to obtain when the isomorphous substances are complex in composition. In a series of simple isomorphous salts where the metals only are replaceable, it would seem that possibility of similarity is greater than in a series of salts of complex composition involving replacement of a group nature. One would thus not expect as great similarity among the etchings of the apatite group as among the calcite group when the members of each in turn are exposed to similar conditions of corrosion; and, considering the chemical properties of the replaceable elements, it seems only natural to expect greater similarity where the metals are chemically much alike. In this connection it may be suggested that atomic volume of replaceable elements in an isomorphous series may play a more important part than

the chemical likeness. On the other hand, a study of the etching of calcite and aragonite shows that the chemical nature of the atom is only one of the factors entering into the problem. This view may account for certain departures from the usual form occasionally witnessed in the etchings of an isomorphous series, and it further suggests an explanation of similar figures, produced under like conditions, on minerals that are not isomorphous. It should be remembered, however, that Retgers does not claim the converse of the law to be true, i.e., that similar etchings always indicate isomorphism. As an example, according to the author's results, the second-order prisms of phenacite (Be_2SiO_4) and willemite (Zn_2SiO_4), when etched by the alkali hydroxides, show similar figures, and yet, according to analyses recorded, the metals Zn and Be do not seem to be replaceable in the orthosilicates. That their chemical properties are related, however, is evidenced by their position in the Periodic Table; and one naturally regards similarity of etchings on such minerals as being attributable in some slight degree to the chemical constituency of the molecule rather than as being in every case the result of accident. It seems probable that the substitution, in the molecular network, of molecules that differ chemically from those of the host, and thus react differently to the solvent, may cause a change in the etchings; but it is not easy to determine how great this change may be. In keeping with this view it would be expected that the variation of the etch figures in an isomorphous series would be no greater than the chemical differences of the substitution elements, and that this difference would vary in degree according to the solvent used and the crystal plane whose etchings were to be compared.

It would seem, then, from the study of a limited number of mineral groups, that on the whole their etchings have many properties in common which suggest a fixed relationship throughout a series of isomorphous compounds. Whether the points above stated concerning chemical difference of the replaceable atoms have any significance here, can only be determined through experiment. It may be that the etchings resulting from replaceable mixtures of elements do in fact register such differences,

but that these differences are too inconspicuous to be detected through mere casual observation. In this case the figures would no doubt be considered similar.

Having treated theoretically some of the more important phases of the etch method, and having called attention to certain matters of interpretation, the author now proposes to deal more specifically with the subject of Etch Figures. In the discussion which follows, the etchings of several important minerals, some of doubtful symmetry, are described in detail and illustrated by means of photographs. A careful study of these will no doubt assist the reader to a better understanding of the method usually employed, and will facilitate interpretation.

CHAPTER VI

THE SYMMETRY OF SEVERAL IMPORTANT MINERALS AS SHOWN BY THEIR ETCHINGS

CUPRITE

In his investigation of crystals of this mineral from Cornwall, England, H. A. Miers [1] reported the occurrence of the pentagonal icositetrahedron (986). Since this time there has been some doubt as to this classification, owing to contrary evidence indicated by its etch figures, and its failure to show optical activity. H. Traube,[2] as early as 1895, pointed out the apparent inconsistency in the physical and chemical data and called attention to the holohedral character of this mineral as shown by the etch pits developed by means of HNO_3 on the octahedral faces. These figures were regular three-sided pyramids having a symmetrical relation to the octahedral edges, in perfect agreement with holohedral symmetry. On the cube and dodecahedron, definite etch figures were not obtained. Additional evidence of the holohedral character of this mineral is to be seen in the arrangement of its atoms as shown by X-ray analysis.[3]

The writer, during a brief study of the etchings of cuprite, has found his results to be in harmony with those of Traube, and, having carried the investigation just a little further to include the three fixed forms, offers these additional data as a minor contribution pointing to the holohedral character of cuprite.

Owing to the ready solubility of cuprite, good results are not obtained unless excellent crystals can be secured and very dilute solvents used in the etching process. Cubical and octahedral crystals from Bisbee, Arizona, and dodecahedral crystals from

[1] Phil. Mag. (5), 18, 127, 1884.

[2] Neues Jahrb. Min. Geol. Beil., Bd. **10**, p. 455.

[3] Tutton A. E. H., Cryst. and Pract. Cryst. Measurement, Ed. 2, 1922, Vol. 1, p. 677.

Moonta, Australia, were found satisfactory for this work, although the latter were much less desirable, owing to slight irregularities of the crystal surface, and proved to be very difficult to etch.

The Octahedron (111)

Well-defined etch pits were obtained on the octahedral faces after immersion in very dilute nitric acid, for a period of several minutes. (See Fig. 7.) The etch figures are perfectly equilateral and composed of three triangular faces having symmetrical positions, indicative of three planes of symmetry. The 60° angles of the figures are turned symmetrically to the octahedral edges, thus revealing no trace of hemihedrism in the molecular configuration of this form. Etchings may also be obtained on the octahedron by adding two or three drops of sulfuric acid to 20 cc. of water, or by adding a few drops of nitric acid to 20 cc. of concentrated solution of ammonium chloride. Any of these solvents will be found satisfactory, except that, in the case of the nitric acid solutions, free copper deposits on the faces of the cuprite which necessitates subsequent washing and brushing before examination can be made. If the ammonium chloride solution is used, much more time is necessary for the formation of etch pits, even to an hour or more, but generally these are very distinct and well formed. The etchings produced on the octahedron by all of these solvents appear to be much the same; if there is a difference in their shape, it must be very slight. The face of the octahedron may occasionally be seen forming the bottom of the pit, but this probably represents a more mature stage of development and is not considered a new type of figure.

The Cube (100)

A great deal of difficulty may be experienced in developing well-defined etch figures on this form. Whether this is due to inherent properties of the cube face, or to the particular crystals used in this investigation, the writer is unable to say; but great care must be exercised when treating the cube with any of the solvents previously mentioned. The best figures are obtained by

very cautious treatment with ammonium chloride solution to which have been added a few drops of dilute nitric acid. The figures so obtained at first appear circular, but with continued growth become regular four-sided depressions, divisible by four planes of symmetry. The boundary lines of the figures make 45° angles with the cube edges, again indicating holohedral symmetry. (See Fig. 7.)

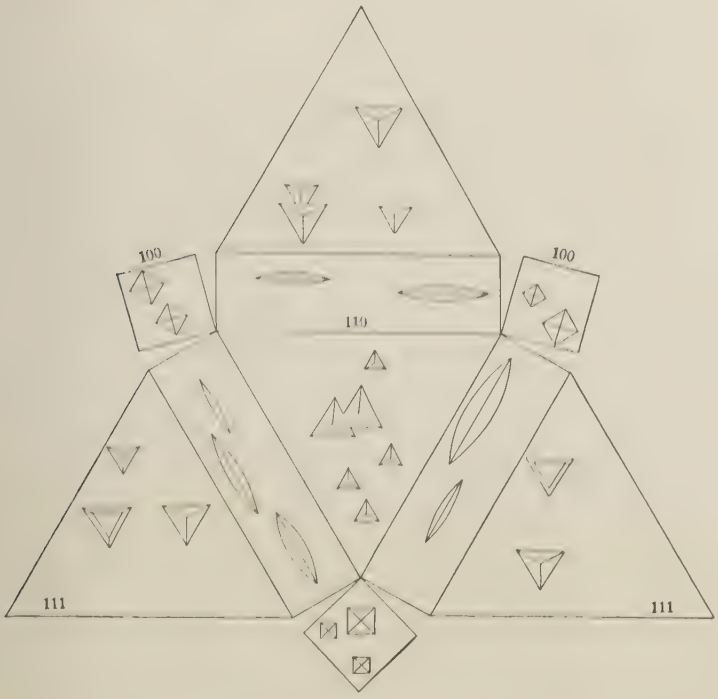


FIG. 7.—Cuprite Etched by Dilute HNO_3.

THE DODECAHEDRON (110)

The dodecahedron occurring in combinations with the cube, from the Bisbee District, does not respond satisfactorily when the cube is etched as stated above. That this is due to the uneven character of the face, rather than to any great difference in solubility, may be observed when simple dodecahedral crystals

from Moonta, Australia, are treated with the same solution with fairly satisfactory results. Dilute nitric acid, sulfuric acid, or ammonium chloride, may be used for etching this form, with very little difference in the shape of the resultant figures. The etch pits are all simple canoe-shaped depressions, elongated parallel to the long diagonal of the rhombic face. (See Fig. 7.) They are divisible by two planes of symmetry cutting the dodecahedral face at 90°, and are so related on adjacent faces as to conform to the holohedral symmetry of the isometric system.

From a consideration of the foregoing data, it would seem that the result of X-ray analysis, the absence of circular polarization, and the holohedral symmetry as shown by the etchings of the three fundamental forms, all point to the holohedral character of cuprite. However, Dr. Wherry [4] called attention to cuprite crystals in the Brush Collection, which had been examined by Goldschmidt and reported to be unmistakably plagiohedral; but he added that the composition of this material is not known. It is possible that other elements, such as silver or thallium, may occur in quantity sufficient to affect the symmetry class. There is also the possibility that cuprite may occur in two phases; it will be remembered that pyrrhotite symmetry also proved troublesome until it was learned that there were two distinct phases dependent upon conditions of temperature. It would seem, therefore, in view of these apparently inconsistent data, that cuprite can well be investigated further.

APOPHYLLITE

Apophyllite is another mineral which exhibits conflicting data, when tested by physical and chemical methods.[5] Its " undoubted biaxial " optical character is in no way in agreement with its crystal form or its holohedral symmetry as revealed by its etch figures; and as yet no wholly satisfactory explanation has been offered for this discordance. A consideration of

[4] Personal communication.

[5] Jaeger, Lectures on the "Principle of Symmetry," p. 179.

crystal form alone may often be misleading, owing to the lack of development of crucial faces which characterize a crystal type, or to complex molecular growth as often exhibited by twinned crystals. The etch figure affords another means of approach, and by the writer is believed to be a reliable check upon the true symmetry of crystals, if caution is used in properly selecting the material and interpreting the results.

Apophyllite has been investigated by means of the etch method. As early as 1885 Rinne [6] described the etchings on three important crystal forms as obtained by hydrofluoric acid, and these are in agreement with the results obtained by the writer. However, additional solvents have been used by the writer to etch this mineral, and the etchings of other forms have been examined. Photographs and descriptions of these etchings follow.

Apophyllite, owing to its ready solubility, requires very dilute solvents, especially since its crystal faces are invariably irregular, being marked by striations and vicinal faces. For this investigation transparent crystals from Paterson, New Jersey, having the usual habit, were found most desirable. The solvents used were hydrofluoric acid, nitric acid, sulfuric acid, and potassium hydroxide fusion. With all of these, solution proceeds with greater rapidity in the direction of the *C* axis and, in the case of sulfuric acid, differential solution is most striking. The basal pinacoid is at once eaten away; but the prism (100) and the pyramid (111) apparently resist the attack of the solvent, and, after prolonged treatment, little if any change may be observed in the character of these forms. In etching the basal pinacoid, dilute sulfuric acid has been found very desirable; for the other forms, hydrofluoric acid yields good results, and all solvents produce etchings which correspond to the symmetry of the holo-symmetric type of the tetragonal system.

Unit Prism (100)

This form is usually well developed and yields to the attack of the solvents, with the result that distinct etchings are obtained.

[6] Neues Jahrb. Min. Geol. Beil. Bd., 1885, 2, p. 19.

Their interpretation, however, is a matter of considerable importance, as two grades of symmetry may be revealed, which may possibly be caused by the striated character of the faces upon which the figures appear or through intergrowths, or development of beaks.

PHOTO 1
Apophyllite (100), Etched by Dilute Hydrofluoric Acid

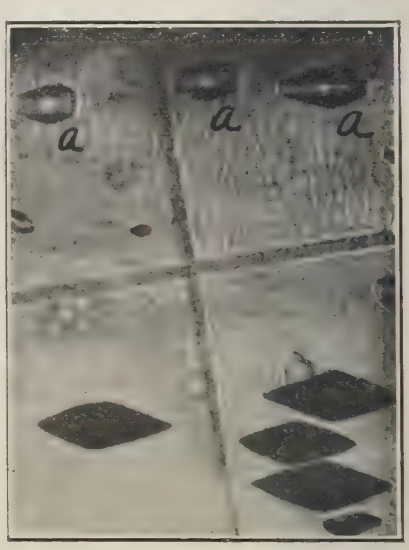


PHOTO 2
Apophyllite (100), Etched by Dilute Hydrofluoric Acid

The figures as obtained with dilute hydrofluoric acid may be seen in Fig. 8 and Photos 1, 2, and 6. The asymmetric character of some of the etchings is easily discernible and at first appears as contradictory evidence; but the great similarity of the figures developed on the ditetragonal prism and the asymmetric figures of the unit form (100) suggests an intergrowth of the etchings through the formation of striations produced by the oscillatory growth of these two forms. As has already been stated, the slightest imperfection of the crystal surface may materially alter the exterior edges of the etchings, and certainly such striations as appear on (100) of apophyllite may prove very troublesome in one's interpretation of the symmetry

of this face. The symmetrical etchings are diamond-shaped, and composed of four pyramidal faces so arranged as to be symmetrical to two planes at right angles, one vertical, the other horizontal.

The distorted figures are quadrilateral and may be monosymmetric or asymmetric, but usually the latter. (See Photo 3.) Hence, from a consideration of the H_2F_2 etchings of this form

Photo 3

Apophyllite (100), Showing Distorted Etchings. Beaks are Plainly Visible.

alone, the true symmetry may be doubted; but there is a preponderance of evidence, obtained by other solvents upon this face and on other forms, which points in the other direction and leaves little doubt as to the real symmetry content. Etchings marked *a* are transitional in character (Photo 2).

If apophyllite be immersed for a few seconds in a water fusion of potassium hydroxide, distinct etchings may be obtained on the unit prism. These are oval in shape and perfectly symmetrical to two planes in accordance with the holo-symmetric type of the tetragonal system. Very few of the etchings possess a

distorted outline. (See Photo 4.) The etchings produced by the potash fusion bear great resemblance to the natural figures subsequently described for this form. The latter, however, are more mature. (See Fig. 9 and Photo 5.)

PHOTO 4

Apophyllite (100), Etched by Alkali Hydroxide

DITETRAGONAL PRISM

The figures of the ditetragonal prism are quadrilateral pits, for the most part symmetrical to the horizontal plane. Like those of the prism adjacent, the anomalous etchings probably have their origin in the uneven striated character of the face, together with the development of beaks previously described. The etchings of this form do not possess a vertical symmetry plane, but are so related on adjacent faces of the form as to agree with the symmetry of the type. There is little difference in the solubility of the prism faces.

Pyramid (111)

This face reacts to the various solvents in a manner very much like the prisms. If it is etched with cold dilute hydrofluoric acid for a period of an hour, very distinct figures are obtained. In their immature stage they are simple isosceles triangles with the base turned to the equatorial edge, but as

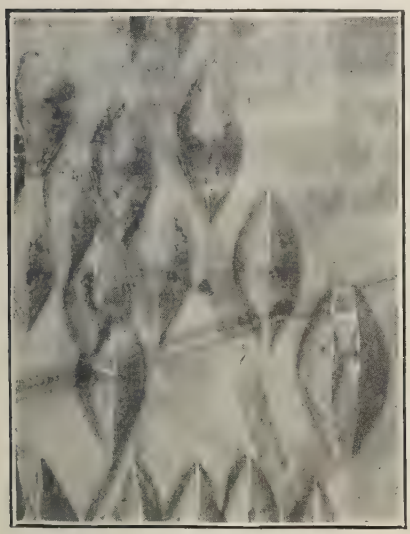


Photo 5
Natural Etchings on (100) of Apophyllite.

Photo 6
Apophyllite (100), Etched by Dilute Hydrofluoric Acid

solution continues a regular quadrilateral pit results, which is perfectly symmetrical to a vertical plane and so oriented on adjacent faces as to correspond with the holohedral symmetry of the tetragonal system. (See Fig. 8 and Photo 7.) Distortion due to beak development is shown in *b*, Photo 7. The potash fusion yields figures which are similar in orientation and differ only in possessing rounded outlines. All normal figures are symmetrical to a vertical plane.

Base (001)

Considerable difficulty may be experienced in etching this form, owing to its easy solubility and imperfect surface. Solution attacks it at once and proceeds with great rapidity, usually resulting in irregular corrosion pits and solution channels, which often extend in directions at 90° to each other. (See Photo 8.) However, sulfuric and hydrofluoric acids were used with fair

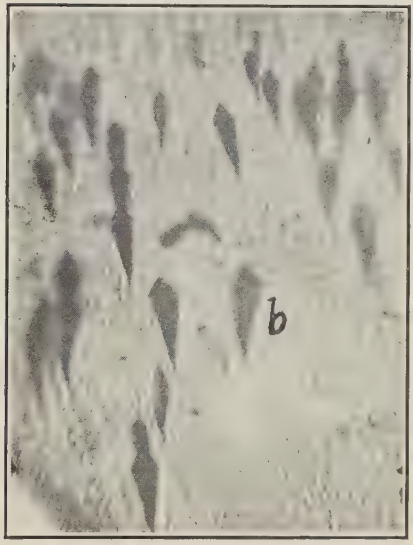


Photo 7
Apophyllite (111), Etched by Dilute Hydrofluoric Aicd.

Photo 8
Solution Channels on the Base of Apophyllite.

success; the figures so obtained are square pyramidal pits with their edges turned 45° to the basal edges. (See Fig. 8.) Some of the figures appear to represent a series of etchings, one contained within another, giving a step effect to the pit. The natural etch figures observed on Paterson crystals differ from the artificial ones only in their position on the face. Unlike the etchings produced by artificial means, these are turned with their edges parallel to the basal edges of the crystal. All figures

examined on the basal pinacoid, whether produced by laboratory solvents or by natural solutions, indicate by their shape and

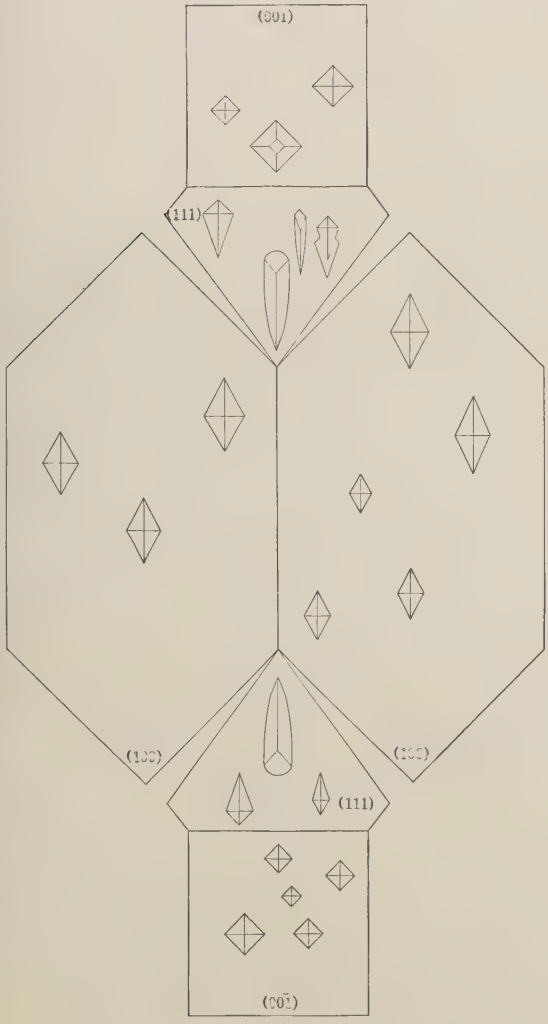


Fig. 8.—Apophyllite Etched by Cold Dilute HF.

position four vertical planes of symmetry, corresponding to the ditetragonal equatorial type.

Thus, from a consideration of the etchings of four forms, among which there is mutual agreement, evidence is set forth which clearly points to the holohedral character of this mineral.

PHOTO 9

Natural Etchings on the Base of Apophyllite. (Cf. Photos 13+14.)

NATURAL ETCHINGS ON APOPHYLLITE FROM PATERSON, N. J.

Natural etch pits were found to occur on three important forms, namely, the base (Photo 9), the unit second-order prism (Photo 5), and the unit first-order pyramid (Photos. 10, 11, 12). These figures are exceptionally large and well defined and afford an excellent means of study. (See Fig. 9.) The symmetry as revealed by these figures is in perfect agreement with the results obtained by laboratory methods and tends to strengthen the view that etchings, even though produced by many different solvents, do not err in their revelation of the symmetry of a crystal. If, upon treatment of a crystal with many different solvents, the results so obtained were found to be inconsistent, one might reasonably doubt that the etch figure does reflect the molecular

arrangement within the crystal; but the results obtained by various solvents, in the experience of the writer, invariably point

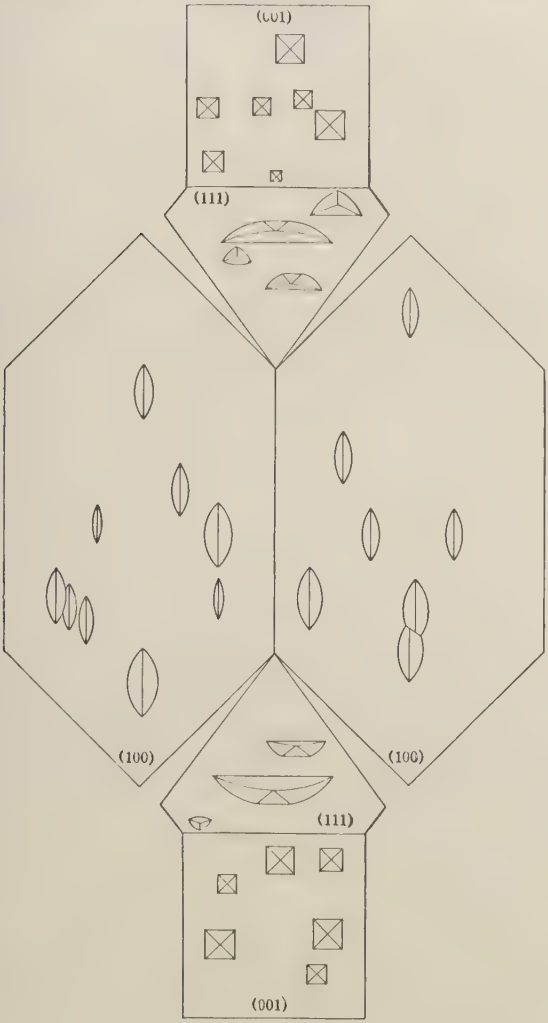


FIG. 9.—Natural Etchings on Apophyllite, Paterson, N. J.

to the same grade of symmetry; and the suggestion [7] that mature etchings are merely surface phenomena certainly cannot

[7] Wherry, Pres. Address, Am. Min., Vol. 9, 1924, p. 53.

be interpreted as meaning that the etch figure, as an indicator of differential solution within a crystal, is incapable of revealing

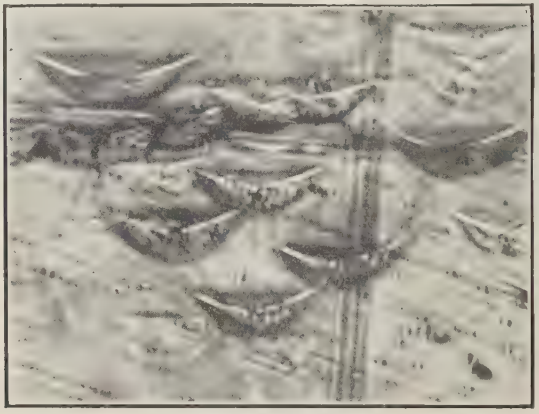


PHOTO 10
Natural Etchings on the Pyramid of Apophyllite

the various interatomic forces, and hence the symmetry. It would seem impossible for a growing crystal possessing a definite

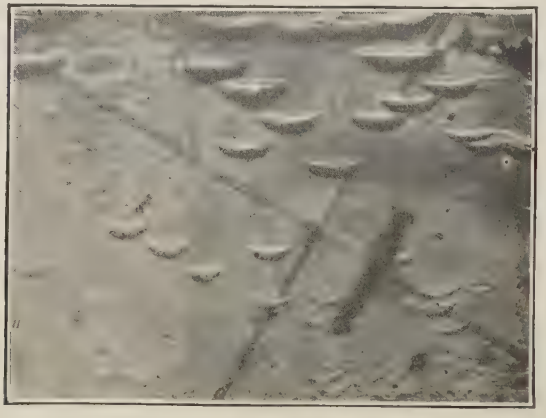


PHOTO 11
Natural Etchings on the Pyramid of Apophyllite.

composition to develop faces other than those which represent the symmetry of the type in which the crystal belongs. Why,

then, should solution, the reciprocal of growth, unlock or inaugurate new forces not in harmony with those constructive forces operative in crystal growth?

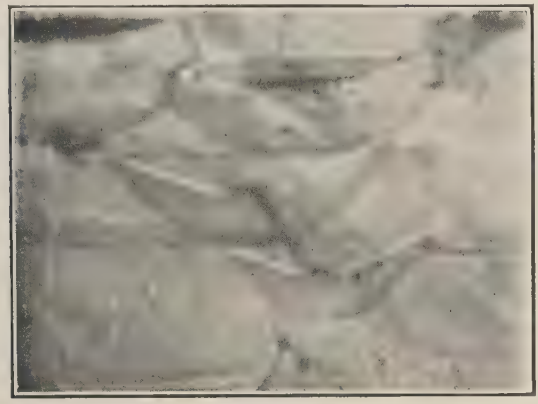


PHOTO 12
Natural Etchings on the Pyramid of Apophyllite.

APOPHYLLITE

SOLUBILITY EXPERIMENT

Period of first immersion, twenty minutes

Four pyramidal crystals of this mineral from the same specimen (Harz Mountains, Germany) were immersed at the same time in the following solvents (cold):

20 per cent HNO_3
20 per cent HCl
20 per cent H_2SO_4

9.8 cc. acetic acid plus .2 cc. H_2F_2

At the end of twenty minutes the following was observed:

(1) *Acetic acid plus* H_2F_2

All faces (base, pyramid and prism) were attacked.

Base became covered with white flocculent efflorescence.

Pyramid faces revealed minute etch pits, the shape of which could not be determined. They were well scattered over the faces.

(2) *HCl*

All faces were attacked.

Pyramid and base were covered with white efflorescence, which after being removed revealed action of the solvent without giving good etch figures.

The prism face was brighter and slightly etched, but figures were too small to be definitely determined.

(3) HNO_3

All faces were attacked in a manner similar to that shown by action of HCl.

The prism seemed to possess a higher luster than the pyramid and gave some indication of growth of distinct etchings.

(4) H_2SO_4

Base violently attacked—more so than by other solvents.

Pyramid and prism showed not the slightest sign of attack.

It is apparent that solution (maximum) is with all solvents that direction parallel to *c*.

Period of second immersion, ten minutes

(1) *Acetic acid plus* H_2F_2

All faces were attacked.

Pyramid and prism covered with minute etchings, the shape of which could not be determined. They did, however, appear to be elongated parallel to *c* on both the pyramid and the prism.

The base was attacked with formation of a white efflorescence, which after being removed with a brush revealed the attack of the acid without definite etch patterns.

(2) *HCl*

All faces acted upon without definite figures. Prism remained bright and gave some promise of figures.

The base acted as in other solvents.

(3) HNO_3

Reaction on all faces very similar to that of HCl. Prism gave promise of figures, but at this stage they were indefinite.

Base most easily soluble.

(4) H_2SO_4

No evidence of attack on any face except the base, which was eaten out, forming a depression, with formation of white jelly-like efflorescence.

Period of third immersion, twenty minutes

(1) *Acetic acid plus* H_2F_2

Under the microscope the figures of the prism were of the shape previously described, but some had an appendage on *one* side only. The appendage appeared to be a development distinct from the figure proper, but practically all figures showed it. One or two did not.

Pyramid faces showed corroded patches which blended rather abruptly into brighter patches bearing minute etch patterns, but which were distinct and individual. Under the microscope these appeared to be identical with the etchings by dilute H_2F_2.

The base revealed no good etchings.

(2) *HCl*

Crystal showed effects of acid, became milky opaque, and crumbled on edges and corners, the whole structure apparently breaking down. The faces, however, were still intact, but no good figures resulted.

(3) HNO_3

Crystal appeared very much as did the HCl crystal. Same indefinite etchings could be seen on the pyramid and prism.

All faces were attacked; base most vigorously.

(4) H_2SO_4

Crystal was unchanged with the exception of more decided corrosion of the base.

Period of fourth immersion, fifteen minutes

(1) *Acetic acid plus* H_2F_2

Etch figures were much more distinct.

Prism was cut by distinct solution channels, usually parallel to basal cleavage; some, less deep, extended parallel to the *C* axis. An important thing to be noticed here was the much larger number of symmetrical figures than occurred in the earlier stages of development.

Pyramid figures were still quite indistinct, but definite and individual. They were elongated parallel to *C* and did not appear to grow quite as fast as those of the prism.

The base revealed no essential difference in its appearance. It showed no figures.

(2) *HCl*

Acid ate in along incipient cleavage cracks, causing crystal to break into thin laminæ. The pyramid faces became dissected by irregular cracks and assumed a milky white appearance which extended for a little way into the crystal, the interior of which remained transparent and glassy. The pyramid faces were semi-lustrous, but revealed no etch figures.

(3) HNO_3

Identically same appearance as HCl crystal. Crystal broke up, became incoherent, cut by irregular cracks, but refused to etch.

(4) H_2SO_4

Basal face gave way to a pit, not definitely bounded.

Pyramid and prism faces were bright and lustrous with no sign of solvent action.

Period of fifth immersion, thirty minutes

(1) *Acetic acid plus* H_2F_2

Faces revealed very little change, except that etchings were better developed, and did not differ essentially from those developed in dilute H_2F_2.

(2) *HCl*

Crystal was corroded and destroyed. Turned to a white flocculent mass. No etchings observed.

(3) HNO_3

Fate of this crystal same as that immersed in HCl.

(4) H_2SO_4

No change—pyramid and prism lustrous and untouched by solvent.

Conclusion

Thus, after one hour and thirty-five minutes' immersion in the four cold solvents above mentioned, only one of the four crystals used revealed definitely etched faces. Two of the crystals were completely destroyed, and the third barely touched in any direction except that of the *C* axis.

HNO_3 and HCl yielded no definite figures, but revealed mutual solubility in all directions. The acetic acid containing 2 cc. H_2F_2 proved to be a very good solvent for etching the pyramid and prism, with excessive solution in the direction of the *C* axis.

Sulfuric acid revealed not the slightest evidence of solvent action upon the pyramid and prism faces, but violently attacked the base.

It would seem, for the four solvents, that the chief or maximum solubility is in the direction of the vertical axis, and that the best etching solution is dilute H_2F_2.

Continued action of the H_2SO_4 for many hours on the above crystals caused complete destruction through excessive lamination.

WULFENITE

Another species, concerning which there has been considerable controversy arising from conflicting data, is wulfenite. Crystallographical, chemical, and X-ray studies have been applied;

but there has been no harmony in the results obtained, nor has any fixed and definite solution been arrived at, with respect to the proper classification of this mineral. Johnsen,[8] in a very exhaus-

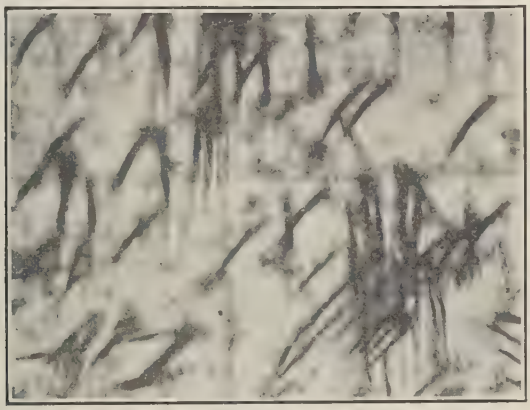


PHOTO 13
Natural Solution Cavities Attached to the Basal Etchings of Apophyllite.
(Cf. Photo 9.)

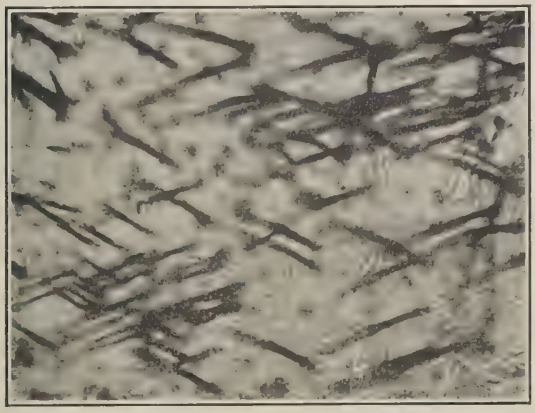


PHOTO 14
Natural Solution Cavities Attached to the Basal Etchings of Apophyllite.
(Cf. Photo 9.)

tive review of published material dealing with the crystal form of wulfenite, and from his own observations upon crystals from

[8] Centr. Jahrb. Min. Geol., 1908, p. 712.

various localities, favors the tetartohedral classification, and suggests that, owing to similar chemical property, scheelite, powellite, stolzite, and other isomorphous species of the group are probably of the tetragonal polar class, identical in symmetry with wulfenite. Traube,[9] thinking that the polar character might be concealed in the mineral scheelite by basal twinning, investigated the etch figures and pyro-electricity and compared

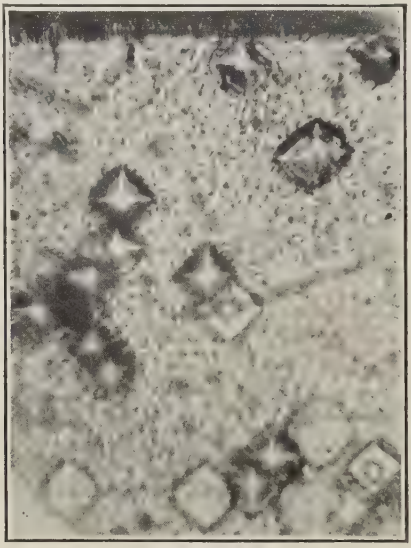


Photo 15
Wulfenite (001), Etched by Nitric Acid

the results with those obtained for wulfenite. Neither of the species showed electrical excitability, and the etchings revealed the same grade of symmetry.

In the etching of wulfenite several reagents were used by the writer, namely, HCl, HNO_3, KOH, NaOH, all of which yielded etch cavities which in shape and distribution were in accordance with equatorial (scheelite) symmetry. The polar development, occasionally exhibited by wulfenite, is thought by Traube to be due to secondary developmental processes, resulting in the

[9] Neues Jahrb. Min. Geol. Beil. Bd. **10**, 1895-96, p. 457.

transformation of earlier-formed tabular crystals into polar pyramidal individuals—a change very often evidenced in the difference of color and physical character. Dickinson [10] attempted to throw a new light upon this question by means of X-ray analysis of the two minerals, wulfenite and scheelite, but, owing to the fact that he was unable to determine with certainty the location of the oxygen atom in the lattice, a consideration

PHOTO 16
Wulfenite (001), Etched by Nitric Acid

PHOTO 17
Wulfenite (001), Etched by Nitric Acid.

upon which the symmetry differences apparently depend, he could arrive at no definite conclusion other than that the minerals were certainly of lower symmetry than holohedral. Some of the important textbooks in mineralogy classify this mineral as tetragonal polar in symmetry. Dana places it in the scheelite class. Additional etch figure data follow, supplemented by photographs by the author.

Small, transparent, lustrous wulfenite plates from New Mexico, and larger tabular crystals from Red Cloud Mine,

[10] J. Am. Chem. Soc., **42**, 1920, p. 84.

Arizona, were found suitable for etching, especially the former, since their surfaces are exceptionally even, and owing to extreme thinness, may be readily mounted and examined beneath the microscope, which is of great aid in the study of etch figures. The crystals are simple in habit, bearing the base and second-order pyramid (102), both of which revealed excellent etchings.

Base (001)

This form may be readily etched by any of the common laboratory acids. Nitric acid is preferable, however, as a soluble lead compound is formed which does not interfere with subsequent study of the etchings. Immersion in hot dilute nitric acid for five minutes is usually sufficient to produce very definite etchings. However, by using a stronger concentration of cold acid, etch cavities can be very conveniently developed beneath the microscope, where the solution can be seen to attack the crystal face, and the etch pits to grow in size. The base bears square etch cavities, which in themselves are symmetrical but are usually bounded by third-order pyramid faces, which indicate a lack of vertical symmetry planes. The position of the figures on the base depends upon the solvent and its concentration, but they are always turned asymmetrically to the crystalline edge formed by the base and the pyramid. (See Photos 15, 16, 17, and Fig. 10.) In the case of nitric (dilute), the angle through which they are turned is approximately 40°; for dilute hydrochloric it is slightly less. Many of the figures are simple pyramidal forms which do not alter their shape with prolonged treatment with the solvent; others become changed through truncation of the pit by means of development of the basal plane. This change may go on simultaneously with increase in depth, resulting in a figure as represented by *a* in Fig. 10. The figures of the upper and lower base are reflections of one another, and little, if any, difference may be observed in the behavior of these faces when subjected to the corrosive action of the solvent, a fact not in agreement with polar symmetry.

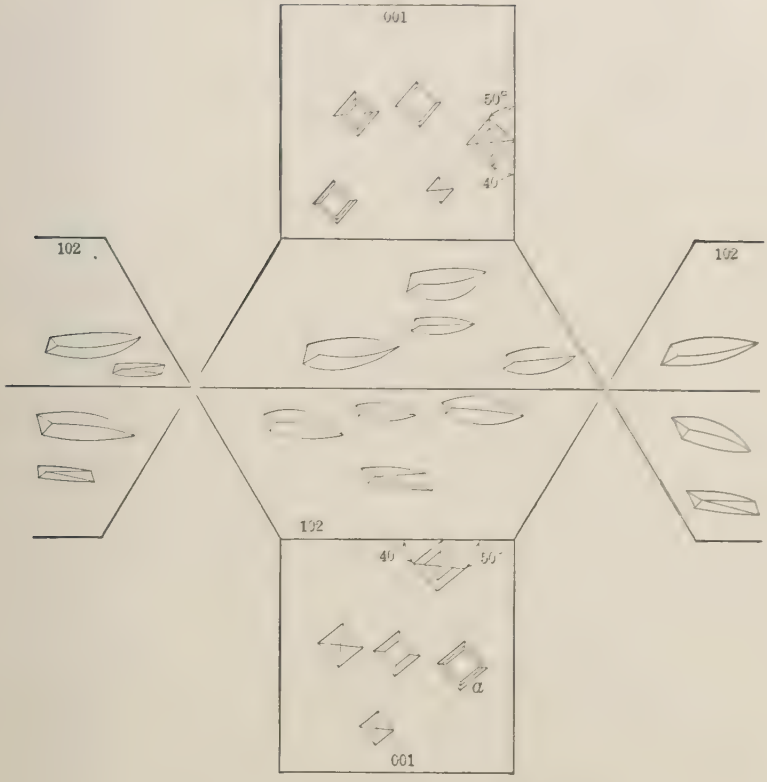


FIG. 10.—Wulfenite Etched by Dilute HNO_3.

THE PYRAMID (102)

This form reacts to the action of the acids in a manner very similar to the base. The etchings produced by HNO_3 are, in the earlier stages of growth, asymmetric triangular pits turned symmetrically to the equatorial crystal edge. With continued solution the figures alter materially to dagger-shaped pits, which are exceptionally uniform and well defined, and by their distribution above and below the equatorial zone point unmistakably to equatorial symmetry. With HCl the figures become more angular. (See Fig. 11.) In the mature stage they are composed of four triangular faces meeting in a common point at the

narrow end of the figure. The etchings are decidedly asymmetric, but, like those produced by HNO_3, their position with respect to the equatorial symmetry plane is such as to indicate equatorial symmetry.

However, up to this point the etch-figure data do not afford final evidence as to the equatorial symmetry of wulfenite, for supplementary twins joined by the base could easily exhibit the same degree of symmetry. But when crystals, bearing the prism, were etched with HNO_3 and NaOH, the results were found to be in accordance with scheelite symmetry. Unfortunately, the prism faces of wulfenite crystals are usually very irregular of surface, being either striated vertically or marked by

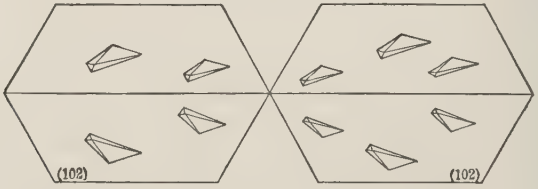


FIG. 11.—Wulfenite Etched by Dilute HCl.

vicinal faces, both of which, however, correspond to an equatorial plane. Regardless of this, a few etchings were obtained which appeared symmetrical to a plane normal to *C*. Owing to very rapid solution of the irregular prism surfaces, the face soon becomes covered with etch hillocks, which likewise indicate an equatorial symmetry plane. Thus, it would seem that wulfenite is tetragonal equatorial in symmetry.

APATITE

An interesting application of the etch method may be observed in the experiments on this species, where apparently holohedral forms are shown to possess molecular hemihedrism. In the case of apatite, as remarked by Dürrfeld, crystals occasionally exhibit a polar development of *C* axis. Some investigation has been carried on with reference to the etching figures of apatite, but these studies have not been as complete as could be desired.

The earlier work was done by Baumhauer [11] on apatite crystals from Knappenwand in Untersulzbachtal. He succeeded in showing the presence of the equatorial plane of symmetry of the unit prism by means of HCl. The etch figures described by him are trapezia elongated parallel to *C* and divisible by the horizontal plane of symmetry. In a later paper [12] he discussed the dependence of the position and shape of the basal figures on the concentration and constitution of the solvent, earlier referred to in this book. Von Dürrfeld,[13] working in Strassburg, reported the following results for the face *m*. Ten per cent warm HCl, acting for five minutes, produced regular trapezia composed of five triangular faces. The largest of these, which he designated as *a*, lay in the position of the third-order prism; the remaining four represented third-order pyramid positions. Slight variations of this figure were also observed. Fifty per cent HCl produces triangular figures composed of three faces, the largest of which is the third-order prism; the other two, lying one above and one below the plane of symmetry, are third-order pyramid faces. The change in concentration of the solvent is here observed to affect the shape of the etchings. With 10 per cent H_2SO_4, Dürrfeld obtained etchings which are in general similar to the HCl figures of Baumhauer and practically identical with those of the writer produced by $16\frac{2}{3}$ per cent H_2SO_4. They are composed of two third-order prism faces and two third-order pyramid faces, with monosymmetrical arrangement. In the more mature forms, a bottom face becomes apparent. Most of the figures are composed of the four faces above mentioned and so placed as to correspond to the symmetry of the type. With 50 per cent H_2SO_4 Dürrfeld obtained no positive results; the prism as well as the pyramid faces became dull. The 10 per cent HNO_3 produced triangular figures which are composed of one third-order prism and two third-order pyramids; the intersections of the latter with the crystal surface are usually slightly curved. The results of 50 per cent HNO_3

[11] Sitzungsber. Akad. Wiss. München, **5**, 169, 1875.
[12] Sitzungsber. Akad. Wiss., Berlin, **42**, 863-78, 1887.
[13] Z. Kryst., **50**, 592, 1912.

on the unit prism do not differ essentially from those of the 10 per cent H_2SO_4 solution; but, for the first time, Dürrfeld observed etchings on the second-order prism, the other solvents not having been active enough to etch this face with the same rapidity as were the unit prism and pyramid faces. The second-order prism reveals a four-sided figure also; all boundaries are straight, the two longer extending parallel to the prism edges. Four faces comprise the figures, the two larger being third-order prism faces; the remaining two lie in positions above and below the equatorial plane, corresponding to the third-order pyramids. Thus the work of Dürrfeld proves very conclusively the presence of the horizontal plane of symmetry in the prism faces *m* and *a*. Aside from this, very little work has been done relative to the etchings of apatite. Hence, the writer has desired to carry the investigation a little farther by examining the etchings of the pyramidal faces and the base, and likewise the prisms *m* and *a* by a variety of solvents of varying concentrations.

Apatite

For the purpose of this investigation, beautiful water-clear crystals from the Austrian Tyrol have been found very satisfactory. They are tabular in habit with the faces *m*, *x*, and *c* the best developed; other forms are *y*, *r*, *s*, and *a*. All forms have a fine luster, quite suitable for etching. A variety of solvents on the various faces have produced a considerable number of fine etch pits, which are described and illustrated in the following paragraphs. The difference in solubility of the various forms is readily observed after brief immersions in almost any solvent, the more common forms etching with greater ease. As a usual thing, the more common hexagonal minerals so far investigated show a marked solubility in the direction of the vertical axis. Five of the fundamental forms were etched, the unit prism being first investigated.

Prism $(10\bar{1}0)$

The form $(10\bar{1}0)$ became beautifully etched after forty-five minutes' immersion in hot concentrated citric acid. (See Photo 18.) The etchings are composed of four or five faces, the largest being triangular and occupying a position in the prism zone. The intersection of this face with the crystal surface is quite curved. Above and below, lying adjacent to this face, are two smaller triangular faces occupying a position in

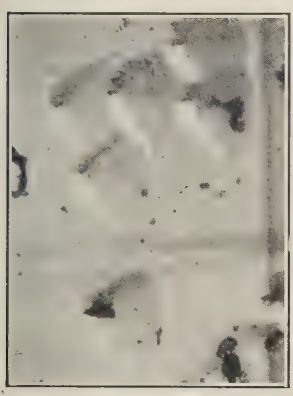


Photo 18
Apatite (1010), Etched by Concentrated Citric Acid

Photo 19
Apatite (1010), Etched by Concentrated Tartaric Acid

the zone (1010)/(1121). The narrow end of the figures may be composed of one or two small triangular faces, the mature figures having two, one above and one below the line of equatorial symmetry, and these lie in the third-order positions. In outline the figures are pentagonal and symmetrical to an equatorial plane. The five faces composing the pit meet in a common point near the narrow end. The figures accord with the symmetry of the type.

Immersion in hot concentrated tartaric acid produces figures which are to a large degree similar to those just described; several distinctions, however, are noticed. (See Photo 19 and Fig. 12.) The tartaric acid figures may be said to be triangular,

with the largest face lying in the prism zone; as in the citric acid figure, the intersection of this face with the crystal surface is curved, but in a lesser degree. This face is very often diminished through the development of a bottom plane, which is very marked in the more mature figures. The faces, one above and one below the plane of equatorial symmetry, are quadrilateral in the presence of the bottom face, and approximate the third-order pyramid position. In most cases these two faces unite to form the narrow end of the figure, but in the very mature

PHOTO 20
Apatite (1010), Etched by Dilute Nitric Acid

PHOTO 21
Apatite (1010), Etched by Dilute Nitric Acid

forms this line of intersection gives way to a small triangular face, lying in the prism zone, and producing a quadrilateral figure. The plane angle bisected by the plane of symmetry passed through the figure measures approximately 82°.

The results of hot 15 per cent HNO_3, acting for fifteen seconds, may be seen in Photo 20. These figures, while generally similar, are quite distinct from those of Dürrfeld, produced by 10 per cent HNO_3. They are composed of four or five faces, the intersections of the lateral faces with the crystal face being curved. The two faces occupying positions above and below the equatorial plane lie in the third-order pyramid position. The large face divided symmetrically by the equatorial plane is

undoubtedly the same form of Dürrfeld. The intersections of the third-order pyramidal faces are often replaced by a small triangular face lying in the prism zone. The more mature figures possess a triangular bottom face, which changes the appearance of the figures very perceptibly, but the symmetrical character is still apparent. Photo 21 represents the results of 10 per cent HNO_3, identical with those obtained by Dürrfeld, and incidentally very similar to the etchings of (1010) of endlichite produced under similar conditions.

PHOTO 22
Primitive Etchings Produced by Dilute Sulfuric Acid on (1010) of Apatite.

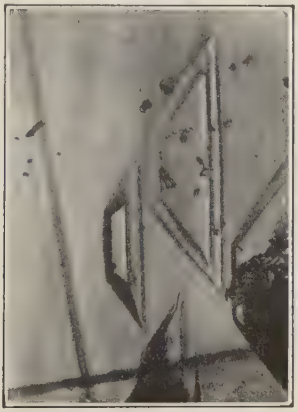


PHOTO 23
Mature Etchings Produced by Dilute Sulfuric Acid on (1010) of Apatite.

A figure quite distinct from any previously described is represented in Photo 22. This etching is the result of warm 20 per cent H_2SO_4, acting for fifteen seconds on a perfect crystal surface. Many acicular calcium sulfate crystals are formed, and partially fill some of the etch pits, making a detailed study rather difficult, unless they be removed by washing in cold water. More mature figures may be seen in Photos 23 and 24. These were produced by $16\frac{2}{3}$ per cent cold H_2SO_4 acting for seven minutes. The outline of the primitive and mature forms is identical (see Photos 22, *a* and 23), but the latter are more complex, owing to greater depth of the pit. The primitive

forms possess little relief, the bottom face being by far the most conspicuous. As solution continues there is a very noticeable increase in the size of the lateral bounding faces, from mere lines or shadows in the primitive to well-developed quadrilateral faces in the mature figures. (See Photos 23 and 24.) This development very often obliterates the dominant face of the primitive form. Four or five faces constitute the mature figure, as the bottom face is absent or present. The largest face is quadrilateral and lies in the prism zone, occupying a position

PHOTO 24

Mature Etchings Produced by Dilute Sulfuric Acid on (1010) of Apatite.

a *b*

PHOTO 25

Mature and Primitive Etchings Produced by Dilute Hydrochloric Acid on (1010) of Apatite.

very similar to the form of Dürrfeld. Lying opposite to this, there may be a smaller face representing another prism. The intersections of these planes with the crystal face are parallel to the prism edges. The smaller faces, lying one above and one below the plane of symmetry, bound the ends of the etch figure and occupy a position corresponding to the third-order pyramid. In outline the figures are regular trapezia, elongated parallel to the *c* axis of the crystal, and symmetrical to an equatorial plane.

The HCl etchings are quite different. Photo 25 represents the unit prism after immersion for fifteen seconds in warm

15 per cent HCl. The mature figures are composed of three faces, one triangular face lying in the prism zone, and two quadrilateral faces one above and one below the equatorial plane. (See Photo 25, *a*.) Two very small triangular faces may appear between these in the very mature forms. The figures have curved boundaries and are elongated parallel to the prism edges; they are symmetrical to an equatorial plane and are more elongated vertically than the etchings of Dürrfeld as produced by 10 per cent HCl. The primitive stage of development is represented in Photo. 25, *b*. If warm concentrated HCl be allowed to act for about ten seconds on the unit prism, the result is a most beautifully etched surface. The figures are of two kinds. (See Photos 26, 27, 28.) Photo 28 reveals the shape of the bottom face. The one illustrated is a simple figure, similar in outline to the mature figure, but has very little depth, the large prism face, so marked in practically all of the other figures, being absent. This is probably a primitive stage in the development. The mature figure is composed of four faces, a large triangular face and a very small quadrilateral face, both lying in the prism zone, and two irregular elongated faces, lying symmetrically above and below the horizontal plane. The margins are quite curved and meet the extremities of the larger prism face, forming sharp ends. The faces are third-order pyramids. If solution be allowed to continue even after the etching has assumed a definite mature form, the deeper portion of the etchings reveal a bottom face, having six sides (see Photo 28), from which there arise almost perpendicularly six small faces, the largest two lying in the prism zone, while the other four approximate third-order pyramid positions. The complex development is indicated in the figure of Photo 26 by the dark central

PHOTO 26
Apatite (1010), Etched by Concentrated Hydrochloric Acid.

portion. The figures are symmetrical to a horizontal plane at all stages of growth. Thus, throughout, there is to be noted a rather constant development of third-order etch faces, indicating the more insoluble zones. Even though a number of different solvents be used, the shape of the etchings, from a symmetry standpoint, is an invariant.

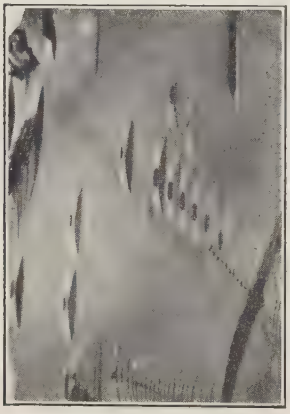


PHOTO 27
Apatite (1010), Etched by Concentrated Hydrochloric Acid.

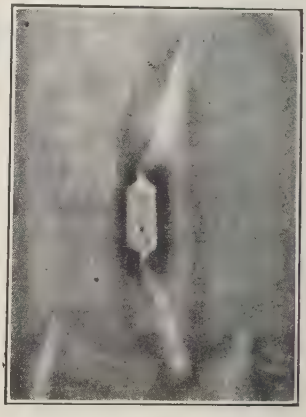


PHOTO 28
Apatite (1010), Etched by Concentrated Hydrochloric Acid. The Pit of the Figure is Plainly Visible.

PRISM $(11\bar{2}0)$

This form is a much smaller face on most of the specimens and is usually more difficult to etch. Fairly good figures have been obtained, however, through the use of tartaric and acetic acids, the stronger acids having been found less satisfactory for this form. Photo 29 and Fig. 12 represent the etch figures of hot concentrated tartaric acid acting for forty-five minutes. The figures, while they are symmetrical to an equatorial plane, are turned in directions opposite to those of the unit prism, and in general appearance resemble the figures occurring on the unit prism of calcite and the orthorhombic sulfates of Ba and Pb—the orientation, of course, being different in the case of calcite. The apatite etchings in the mature stage possess four faces, two

lying in the prism zone, corresponding to the positions of the prisms of Dürrfeld as produced by 50 per cent HNO_3, and two triangular faces symmetrically placed one above and one below the equatorial plane, and corresponding in position to the third-order pyramid of Dürrfeld. The largest face is triangular and lies in the prism zone, its intersection with the crystal face being an indefinite straight line parallel to the prism edge. The face lying opposite in this zone is much smaller and four-sided. In the primitive figures this face may be triangular, but the position remains the same. All of the primitive forms are attenuated normal to the vertical axis, a solution phenomenon which is exceptional in apatite; but as solution continues the figures broaden vertically. There is no bottom face that commonly appears in the forms of the unit prism, and the bounding lines are straight. The two parallel vertical boundaries are intersected above and below the equatorial planes by the pyramidal bounding lines at an angle of approximately 100°, which produces a symmetrical figure in accordance with the apatite type.

PHOTO 29
Apatite (1120), Etched by Concentrated Tartaric Acid.

The 15 per cent acetic acid figures are quite similar to those of tartaric acid described above. (See Photos 30 and 31.) The orientation is the same, and etchings of both acids are composed of four faces similarly placed, but the acetic acid forms are less definite and are elongated parallel to the prism edges, rather than at right angles. While the mature figures are very distinct, the longer vertical boundary is barely visible, as may be seen from Photo 30 or 31. They resemble the HNO_3 forms described by Dürrfeld and accord with the symmetry of the type. The relative solubility of the two prisms is illustrated in Photo 31. The etching at either side of the photograph is that of the $(10\bar{1}0)$ face, the central portion is that of (1120). The small pits may

be observed scattered over the $(11\bar{2}0)$ form, while the surface of the unit prism presents a corroded appearance. The individual nature of the second-order form is thus apparent, both from its reaction to acids and from its etching figures. However, as in the unit form, the molecular configuration conforms to equatorial symmetry.

PHOTO 30
Apatite (1120), Etched by Dilute Acetic Acid

PHOTO 31
Apatite (1120), Etched by Dilute Acetic Acid.

UNIT FIRST-ORDER PYRAMID

On most of the specimens the $(10\bar{1}1)$ form was fairly well developed and etched without much difficulty. The solubility of this pyramid face differs but little from that of the unit prism, which is always the first form to yield to corrosive agents in such a manner as to produce definite etch figures. Very often, other pyramid faces, occurring in the first-order zone, very perceptibly yield to the various solutions after only brief immersions, but the result is a frosted or corroded surface and not a definitely etched one. Occasionally the rarer forms existing on the specimens assume this frosted appearance immediately, and then reveal a few ill-defined individual figures as solution continues. Such surfaces, however, are not satisfactory, and the figures

produced are usually too irregular to reveal accurately the symmetry of the face. This fact is clearly brought out in the action of tartaric acid on the various faces in the first-order pyramid zone of apatite. The forms (1011), (2021) and (3032) assume a dull appearance as does also the third-order pyramid (3141), but the writer is not inclined to recognize this as excessive solubility. The unit pyramid, however, under these conditions, becomes beautifully etched. The same thing is true to a certain degree of the prism zone, but here the second-order prism reveals scattered etchings more or less irregular and varying in size; the first-order prism etches very distinctly, and the third-order prism, which is rarely present, does not etch at all. With tartaric acid there appears to be but little difference in the solubility of the first- and second-order pyramid faces; at least it is nothing comparable to that exhibited by the prisms of these orders. Photo 32 illustrates the figures produced on (1011) and ($11\bar{2}1$) of apatite after immersion in hot concentrated tartaric acid for a period of twenty-five minutes. The corroded pyramid faces of the first-order zone may also be noticed in this photograph. The etch figures of the first-order unit pyramid are triangular in shape, almost identical with the unit-prism figures by the same solvent (*cf.* Photos 19 and 32, *a*). The prism figures are likely to become a little more complex in the mature stage of development, owing to the formation of two curved surfaces partly enclosing the deeper portion of the pit. The pyramid figures, while they are apparently divisible by a symmetry plane bisecting the larger face, are so oriented as to indicate the asymmetrical character of the face. The relation of the figures of the two faces to each other and to the crystalline edges

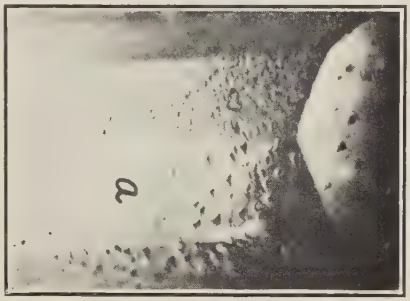


PHOTO 32

Apatite Showing Variable Solubility of the Pyramid Faces, when Immersed in Tartaric Acid.

is represented by Fig. 12, where the hemihedral symmetry is illustrated.

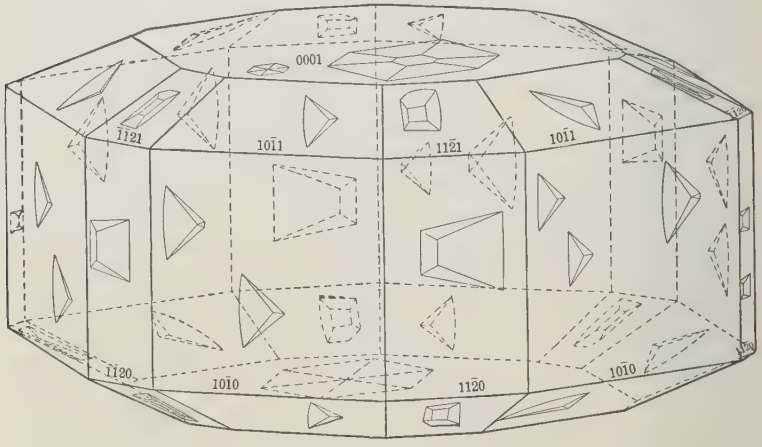


Fig. 12.—Apatite Artificially Etched, Tartaric Acid, Time, Forty-five Minutes.

Unit Second-order Pyramid (1121)

This form is usually well developed and has a good surface. The molecular arrangement of this face, however, is entirely different from that of the first-order pyramid just described, as is indicated by comparison of the etching figures of tartaric acid. (See Fig. 12.) Photo 33 represents the etching produced by concentrated hot citric acid after two hours' immersion. This figure is quadrilateral and composed of five faces, the two larger lateral faces, occupying positions which approximate the unit pyramid, and two lateral faces, the one adjacent to the base being a second-order pyramid, and the face opposite a third-order pyramid; the four intersect the bottom face, which is apparently parallel to the crystal

Photo 33

The Second Order Pyramid of Apatite Etched by Hot Concentrated Citric Acid.

face $(11\bar{2}1)$. The figures are oriented with the narrow end towards the base and opposite in direction in regard to the (1010) figures made by the same solvent. The figures are asymmetrical in outline but become congruent by reflection over the equatorial plane, with the etchings of the corresponding form on the opposite termination of the crystal. This accords with the symmetry of the type.

Hot 20 per cent HNO_3, acting for thirty-five seconds, produced figures on (1121) which are entirely different. (See

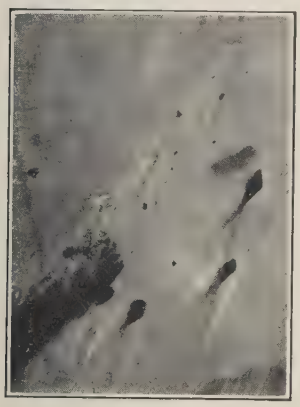


PHOTO 34

The Second Order Pyramid of Apatite Etched by Dilute Nitric Acid.

PHOTO 35

The Second Order Pyramid of Apatite Etched by Dilute Nitric Acid.

Photos. 34 and 35.) These etchings are elongated vertically and composed of three faces, two of which are quadrilateral, acute at one end and having a blunt termination at the other, and one triangular face lying in the zone of the second-order pyramid and the second-order prism. The longer margins of the figure are curved outward slightly, but the curvature, being greater on one, produces an asymmetrical etching. The narrow end of the figure turned toward the base is very distinct, but the limiting margin at the opposite end is hardly visible. The figures in themselves are asymmetrical, but, by their corresponding positions above and below on opposite ends of the crystal, the presence of the diametral symmetry plane is indicated.

Base (0001)

The tabular apatite crystals from the Tyrol, Austria, offer fine opportunities for the study of the etchings of this form. It is a very soluble face and usually etches rapidly with numerous distinct hexagonal pits, which differ only in the smallest detail and in orientation as the concentration or the constituency of the solvent is varied. In the case of tartaric or citric acids, which are very weak, immersion for a period of one-half hour

Photo 36
Apatite (0001), Etched by H3½ Concentrated Tartaric Acid.

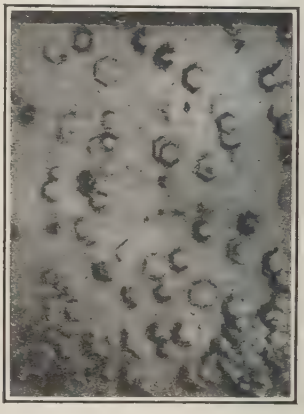


Photo 37
Apatite (0001), Etched by Hot Concentrated Tartaric Acid.

or even two hours for some forms has been found necessary. In hot concentrated tartaric acid beautiful etch figures were obtained after an immersion in the solvent of thirty minutes. (See Photos 36 and 37.) The resultant etchings are of two kinds, the pyramidal pointed, and the pyramidal truncated; in the latter the apex is replaced by a basal plane, which may be large or small. The figures are consequently composed of two forms, the hexagonal pyramid of the third order, and the base. The orientation of these forms approximates an angle of 27° with the second-order position. Hot concentrated citric acid, acting for one and three-quarter hours, etched the base with many distinct forms. (See Photo 38.) The primitive forms

differ from the mature in the presence of a large basal plane and bounding lines which are slightly curved. All of the mature figures are pyramidal, and the apex is never truncated. The figures approximate an angle of 24° 30′ with the second-order position. Very rarely, one may observe an asymmetrical form which appears as an elongated octagon; this is only an intergrowth of several figures lying in the same line and is the origin of the many solution grooves which may be seen cutting the base

PHOTO 38
Apatite (0001), Etched by Hot Concentrated Citric Acid.

PHOTO 39
Solution Channels on the Base of Apatite.

in different directions. (See Photo 39.) These canals, as they have been designated by some writers, may arise from two sources. There may be a series of figures lying in a straight line, possibly a line of secondary cleavage, but not necessarily so, and so spaced that development produces intergrowth on two sides only; this means of formation of solution lines is illustrated in calcite. Again, a single figure may, through rapid solution in one direction, traverse the entire crystal face during a few minutes' time if the substance is a soluble one; this is also illustrated on the prism face of calcite. Both methods of development are exhibited on the base of apatite. The solution lines are not necessarily straight lines, for very often symmetrical

curves are described on the various faces of the crystal. These are often difficult to explain.

The figures produced by 15 per cent hot HCl, acting for ten seconds, are not unlike the etchings just described. (See Photo 40.) The shallow and the deep forms occurring on the other crystals are present here, as are also the solutional canals. The orientation alone characterizes the HCl etchings, the angle varying but one degree from the symmetrical position. The

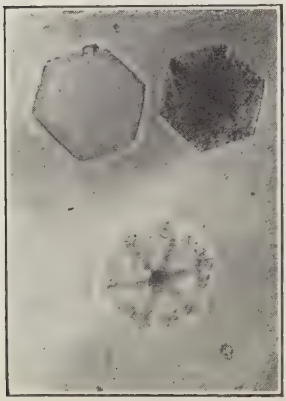


PHOTO 40
Apatite (0001), Etched by Dilute Hydrochloric Acid.

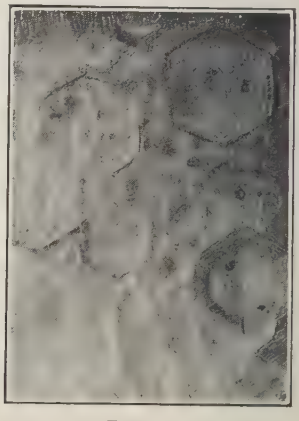


PHOTO 41
Sculpturing on the Base of Apatite.

results of hot 15 per cent HCl acting for thirty-five seconds are illustrated in Photos 41 and 42, where the unusual sculpturing of the basal pinacoid may be seen. Many small figures may be seen within the larger ones.

If equal parts of HNO_3 and HCl are mixed and diluted to 10 per cent, the etchings resulting from fifteen seconds' immersion are very distinct and are oriented 4° out of the symmetrical position. (See Photo 43.) In many of the more mature forms, the " spider web " effect is very apparent; it is produced by a series of small faces lying parallel to the basal plane, or appearing as terrace formations completely surrounding the interior of the figure.

From the foregoing investigation it is readily observed that apatite is hexagonal equatorial in symmetry, a result in accordance with X-ray studies. The variety of figures produced on the prism faces by various solvents indicates very conclusively the presence of the medial plane; moreover, these figures, if turned 60° about the vertical axis of the crystal, become congruent, indicating an hexagonal axis of symmetry. Fig. 12 is intended to show the results of forty-five minutes' immersion in hot con-

PHOTO 42
A Well Developed Hydrochloric Acid Figure on the Base of Apatite.

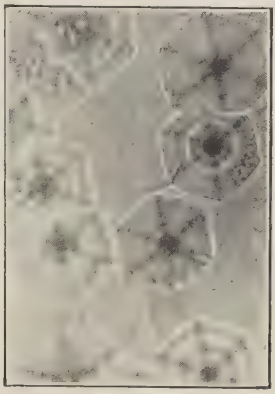


PHOTO 43
Apatite (0001), Etched by Nitro-hydrochloric Acid.

centrated tartaric acid, in so far as position and shape of figure are concerned. The relative size of the figures on different forms, considered as an indicator of the relative solubilities of the various faces, has been disregarded in this drawing; as a matter of fact, certain figures have been enlarged for emphasis, the primary purpose of the diagram being to illustrate the etchings of the crystal as a whole and to show the relation which exists between the orientation and shape of the figures and the crystalline edges.

Endlichite

Beautiful yellow prismatic crystals of endlichite also reveal symmetry of apatite type, and, since there has been no previous investigation of its etchings, the following may be of interest. The specimens etched usually have two prisms $(10\bar{1}0)$ and $(11\bar{2}0)$ with the former the better-developed face. All of the larger crystals are striated vertically, but the smaller specimens are quite smooth and bright. Endlichite, being an isomorphous mixture of lead chloro-vanadate (vanadinite) and the lead chloro-arsenate

Photo 44
Endlichite (1010), Etched by Dilute Nitric Acid.

Photo 45
Endlichite (1010), Etched by Dilute Nitric Acid.

(mimetite) behaves like these species when immersed in nitric acid; the etchings on the unit prism are, however, quite characteristic. Fifteen per cent cold HNO_3, acting for twenty-five seconds, gave numerous well-defined figures (see Photos 44 and 45), which are in no way similar to apatite etchings. In the primitive form they appear circular and have very little depth; but as solution continues they gradually become oval, revealing one very prominent face lying in the prism zone, and adjacent to this, above and below, a triangular form, apparently the third-order pyramid. Occasionally a second small prism face, steeper than the large form mentioned above, may be observed; but this

is usually invisible, because that portion of the pit is overshadowed. Some of the figures appear to be striated in a circular manner; others have radiating striæ issuing from the pit of the figure. Exceptional etch figures have a larger bottom face which produces a figure of less depth. All margins are curved, and the figure as a whole is divisible by the horizontal plane of symmetry, which indentifies this species with the apatite type.

Ten per cent hot nitric acid, acting for five seconds on this form, reveals but little difference in the etch figures. (See

PHOTO 46
Endlichite (1010), Treated with Dilute Nitric Acid for only Five Seconds.

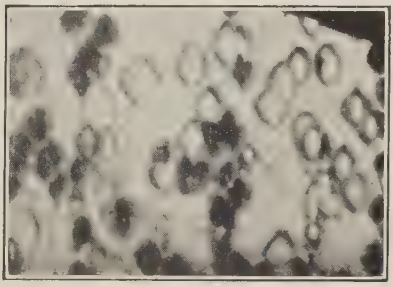


PHOTO 47
Endlichite (1010), After Five Hours' Immersion in Hot Concentrated Citric Acid.

Photo 46.) There is not that striated appearance which is so marked in the 15 per cent nitric acid figures, and the forms in general outline tend toward triangles rather than oval pits. The large prism face mentioned in the 15 per cent figures is even more prominent in these etchings, and the lines of intersection of the four faces are more sharply defined.

As there is a marked chemical difference between nitric and citric acids, some difference should be expected in the etch forms resulting from these two solvents. Five hours' immersion in hot concentrated citric acid was necessary before distinct forms

could be obtained. (See Photo 47.) The outline is readily observed to be distinctly more angular, approximating the rhomb in shape. In fact, many of the bottom faces are roughly rhombic with all angles rounded. The primitive figures appear more angular as solution seems gradually to round out the forms, and the rhombic face of the primitive figure gradually contracts in a direction at right angles to the vertical axis of the crystal until, in the very mature stage of growth, it becomes a mere line. Many of these figures, like those of the stronger nitric acid, are striated, but only the mature etchings show this. All figures accord with the symmetry of the type. The end-lichite specimens are very poorly terminated, consequently the pyramids could not be investigated with any degree of success; the second-order prism, although quite well developed, could not be etched with any certainty, the acids having merely a corrosive effect. The prism etchings, like those of apatite, conform to hexagonal equatorial symmetry.

ETCHINGS ON TOURMALINE

The etching figures of this important mineral have been described by several authors, the majority of whom have agreed on its ditrigonal polar character. It should be noted, however, that a lower symmetry was earlier suggested, especially by Ramsey, Solley, and Jerofejew,[14] but these observations have long since been shown to be incorrect. Baumhauer,[15] through the use of caustic potash, was able to secure very distinct figures on the rhombohedron *R*, and the hexagonal prism *a*. The etchings of the former are triangular pits with the smallest angle turned upward and divisible by a vertical plane of symmetry; the latter contains many asymmetrical triangular forms, which, by their relative positions on adjacent faces, indicate the presence of the vertical symmetry plane passed through the prism edges. T. L. Walker,[16] in working out the physical difference of parallel faces of certain triclinic species, also inves-

[14] Neues Jahrb. Min. Geol. Beil. Bd. **10**, 1895-96, p. 460.
[15] Neues Jahrb. Min. Geol., 1876, 3.
[16] Am. J. Sci., **5**, 178, 1898.

tigated the upper and lower bases of tourmaline which he showed to be two distinct forms. Highly polished basal sections were immersed in red hot fusion composed of potassium bisulfate and coarsely powdered fluorspar for ten minutes, and then withdrawn and treated with hot dilute HCl in order to dissolve the fusion adhering to the plates. This process produced definite etch forms, triangular in shape, and regular. Those on the upper base (0001), are sharply angular with all boundaries straight; on the lower base (0001), the forms are also triangular and similarly oriented, but the sides are curved and the angles blunt, closer observation revealing nine sides similar to a basal section of the crystals. Both faces are compelled to meet the same symmetry requirements, hence the physical difference is slight but is shown to exist. Traube,[17] having secured suitable crystals from the mineral collection of Pech in Berlin, succeeded in etching the forms $(11\bar{2}0)$, $(10\bar{1}1)$, $(000\bar{1})$, and (0001). He made no distinction in the form of the etchings of the two bases as produced by potassium hydroxide, but noted the difference of orientation, those of one face becoming congruent with those of the other after a revolution of 180° about the vertical axis. The figures on the $(10\bar{1}1)$ form are less abundant and composed of three faces, two triangular and one quadrilateral. Some are isosceles with an angle of 100°–110° at the apex. The figures are symmetrical to a vertical plane.

The prism $(11\bar{2}0)$ theoretically possesses asymmetrical figures which reflect those of adjacent faces, owing to the presence of the vertical plane of symmetry cutting the intermediate crystallographical axes. Traube, however, observed symmetrical and asymmetrical figures on the same face but attributed this distortion to the intensely striated surfaces.

Worobieff,[18] in a very exhaustive treatise on tourmaline, involving a study of many hundred crystals from many localities, failed to find sufficient evidence to warrant the previously suggested rhombohedral tetartohedrism. The etching figures, as well as the facial arrangement, point to ditrigonal polar

[17] Neues Jahrb. Min. Geol. Beil. Bd. **10**, 461, 1895-96.
[18] Z. Kryst., **33**, 1900, p. 451.

symmetry. The etchings of the terminating faces, as described by Worobieff are similar in many respects to those of Traube. The prisms yielded indefinite results.

Since the writer concluded his studies of the etchings of tourmaline, a short paper,[19] bearing on the solution phenomena of this species has appeared; it is mentioned here for the sake of completeness. An important point, however, brought out in this paper, is the unlike solubility of the two basal planes. When treated with KOH fusion, the (0001) face bore triangular etch hillocks, but the opposite face appeared much less soluble, finally revealing six-sided etch pits. The results of solution experiments on tourmaline spheres were decidedly confirmative of this solubility difference. After twenty-five minutes' immersion in the KOH fusion, the antilogous pole had been dissolved away nearly to the center of the sphere; the opposite pole was but little affected at this stage of solution. The fact that etch hillocks have not been previously reported on the base of tourmaline probably finds explanation in the failure of investigators to use excessively strong solvents. It is generally considered that etch hillocks indicate rapid solution. However, if solvents of medium strength are used and conditions are well under control, solution may be checked before hillocks appear, in which case the face would yield etch figures. Hence, it becomes a matter of etching conditions, often governed by the length of time through which etching continues. The trigonal pyramid and the prisms did not yield definite results.

The author has investigated three of the forms occurring on gem crystals from Haddam Neck, Conn., which are green, transparent crystals, prismatic in habit and terminated at one end by the trigonal pyramid; the hexagonal prism of the second order, the trigonal prism, and the unit trigonal pyramid were etched.

Trigonal Prism

This form yielded very distinct etchings with sodium hydroxide and also with a 2 : 1 mixture of potassium bisulfate and

[19] Ber. Ges. Wiss., Leipzig, **72**, 1920, p. 48.

powdered fluorspar. Hydrofluoric acid failed to attack it to any great degree. It was found necessary to exercise a little precaution when etching with the hydroxide fusion, as this substance attacks the crystal so readily that a corroded surface results if solution is allowed to proceed too rapidly or is continued too long. To insure good results, the sodium hydroxide is melted, and, before it is heated to red heat, a little water is added, and this solution allowed to simmer, over a weak Bunsen flame; one-half hour is sufficient to produce distinct etch figures. (See Photo 48.) This etching is polar in character and composed of six faces arranged in pairs, with the principal elongation parallel to the prism edges. The two larger faces meet to form the basal groove, which extends lengthwise of the figure and divides it symmetrically. These faces lie in the prism zone. The two triangular faces forming the acute termination of the figures also form a continuation of the basal groove and lie in the zone of the ditrigonal pyramid. The opposite termination is blunt and composed of two small faces, lying one on either side of the groove and dipping at a very sharp angle from the crystal surface. The contour of the mature figures is quite straight, but in the primitive stage the figures are long and narrow with curved contours. All etchings reveal a polar development and indicate a vertical plane of symmetry through the face of the crystal.

PHOTO 48

Etchings on the Trigonal Prism of Tourmaline as Produced by Sodium Hydroxide Fusion.

The trigonal prism of tourmaline becomes well etched after an immersion of ten or fifteen minutes in a red-hot fusion of potassium bisulfate and powdered fluorspar. (See Photo 49.) The figures, like those of the sodium fusion, are polar and

elongated parallel to the prism edges. They are composed of three faces, the two longer ones lying in the prism zone and intersecting to form the basal groove, similar to that described above. The two faces forming the acute termination of the sodium figures are absent in the etchings produced by the bisulfate-fluorspar fusion. The blunt end of these figures is composed of a single triangular face, whose apex meets the basal groove, and whose intersection with the crystal face is a straight line. The contour is less curved than that exhibited by the hydroxide figures. As in the latter, the chief etch zone is that of the prisms. All figures are symmetrical to a vertical plane which accords with the trigonal prism of tourmaline.

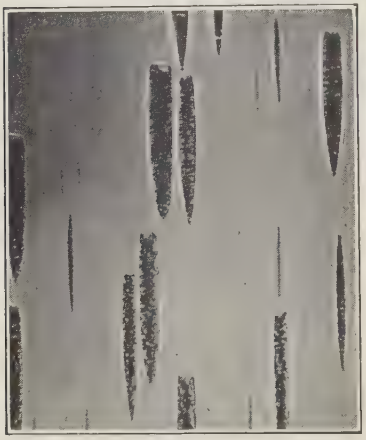


PHOTO 49
Simple Etchings Produced by Potassium Bisulfate–Fluorspar Fusion on the Trigonal Prism of Tourmaline.

HEXAGONAL PRISM OF THE SECOND ORDER

The hexagonal prism does not act unlike the trigonal prism when immersed in the sodium hydroxide and potassium bisulfate fusions; the figures develop with the same rapidity and are as distinct and well formed as those occurring on the trigonal prism. The manner of growth from the simple shallow figures to the deeper and more complex forms, which was observed on the trigonal prism, may also be applied to the etchings of the second-order form. One-half hour's immersion in fused sodium hydroxide gave very distinct etch figures with a polar development and elongated parallel to the prism edges. The figures in the earlier stages of development bear the outline of the mature forms, but have very little depth; a face lying parallel to the crystal face is by far the most prominent, the lateral faces

appearing only as lines. The figures reveal the asymmetrical character of the crystal face at all stages of development, the most complex figures being composed of four faces; the two larger faces lie in the prism zone, but do not dip symmetrically to the bottom of the figures, and these, being also unequally developed, produce an asymmetrical etching. (See Photo 50.)

PHOTO 50
Tourmaline (1120), Etched by Sodium Hydroxide Fusion.

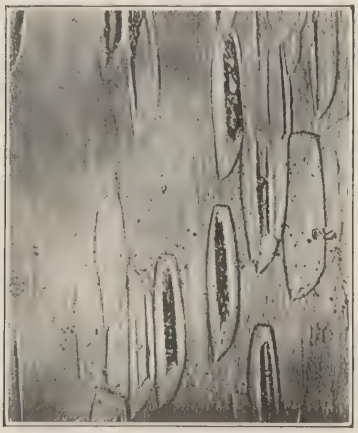


PHOTO 51
Tourmaline (1120), Etched by Potassium Bisulfate–Fluorspar Fusion. Primitive and Mature Figures are Visible.

Another crystal gave similar results after ten minutes' immersion in a red-hot fusion of potassium bisulfate and fluorspar. Primitive and mature figures alike reveal the asymmetrical character of the face. The results obtained differed from those of Traube [20] in that not one symmetrical figure could be observed among the great number of etchings occurring on the face. There is no appreciable difference between the figures of the two solvents except the presence of the more curved contours of the potassium bisulfate figures (*cf.* Photos 50 and 51). All of the figures developed on the prism faces indicate more rapid solution parallel to *c*.

[20] *Loc. cit.*, p. 461.

Unit Trigonal Pyramid

This form is more soluble than either of the prisms and, unless the face is very smooth, it becomes corroded and marked by many solution grooves intersecting at various angles. A few distinct etchings were obtained by means of the potassium bisulfate-fluorspar fusion, after many unsuccessful attempts. The figures resemble those described by Traube and indicate a vertical plane of symmetry. The less common crystal forms being absent from the material used for these experiments, the investigation of tourmaline must of necessity be delayed indefinitely; but it is hoped that the desired forms may be obtained and the results published in the future.

CELESTITE

The etchings of celestite have been examined by several authors. Artini [21] observed the etch forms (326) and (562) on celestite from Romagna. Prendel,[22] in Odessa, etched the forms (011), (102), (001), occurring on crystals from Dorfe, Dorobany, Chotin, with hot conc. H_2SO_4. He obtained on (011) etchings which are tongue-shaped and monosymmetric, similar to natural figures found on barite from Puy-de-Dôme. On (102) they appear as fan-shaped forms, with base turned to the edge (102)/(102). The faces (001) possess rhomboidal pits whose longer diagonal extends parallel to the brachyaxis. The crystals, having been first treated with potassium carbonate and then immersed in HCl, gave etchings on (011) and (102) of the same shape as produced by H_2SO_4, but the face (001) revealed spindle-shaped etchings elongated parallel to the macroaxis. J. Samojloff [23] described natural etchings on celestite from the Isle Nicholas (Aralsee). On (011) he observed equilateral triangular pits. On crystals from Axintikom (Uruchschlucht) etc., he described etchings on (102) which are also triangular. On (110) the etchings are of the same shape and orientation as

[21] E. Artini, Z. Kryst., **25**, p. 390.
[22] R. Prendel, Z. Kryst., **30**, p. 319.
[23] J. Samojloff, Z. Kryst., **45**, p. 117.

those described by Tschermak, on barite. S. Popoff [24] observed natural etchings on (011), of celestite from Berge Lyssaja in Theodosia (Taurien) which are similar in shape and orientation to those described by Samojloff. Samojloff also examined crystals from Put-in-bay, Lake Erie, and found the following etched faces, *c* (001), *o* (011) and *d* (102); *m* (110) was corroded and yielded no distinct figures. The base (001) bears figures which are identical with those described by other authors. On (102) occur symmetrical forms. Some anomalous etchings occur; these are similar to those noticed on the base but have no definite position on the crystal face. They usually appear as triangular continuations, very unlike the etch figures themselves, from which they extend as hollow or flat formations, far surpassing in size the etchings of the face. These anomalous forms are similar to those on (110) of barite as described by Beckenkamp. On crystals from Gloucestershire, England, contrary to all former observations, Samojloff found on (011) several well-defined triangular figures, very much elongated, with the apex turned to the edge $(01\bar{1})$ (011). Symmetrical and asymmetrical figures occur on the same face, the latter being the result of unlike development of the bounding faces of like form in the etching, a solution result similar to that referred to by the writer in discussing transitional growth of apophyllite etchings. Kraus and Hunt [25] have described natural etchings, on celestite from Put-in-bay. The following forms bear natural etchings: (011), (001), (102), (110). The face (011) possesses quadrilateral top-shaped etchings with point turned to the base of the crystal and symmetrical to a vertical plane. The base (001) bears rectangular figures which are symmetrical to two planes at right angles. The dome (102) is marked by regular trapezia with the longer sides adjacent to the edge (102)/(001). The etchings on the prism (110) are similar to those found on (011), but are so oriented as to be symmetrical to the diametral plane.

For investigation of the artificial etchings of celestite, Samojloff used transparent colorless crystals from Racalmuto,

[24] S. Popoff, Bull. Natural., Moscow, 1906, 20, 182 (russ.).

[25] Am. J. Sci., **21**, p. 244, 1906.

Sicily, and from Bristol, England. Those of the former locality are elongated parallel to the brachyaxis and possess a very peculiar sculpturing. (See Fig. 7, Plate IV, Z. Kryst., 45, 1908.) For results obtained with H_2SO_4, HCl, and K_2CO_3 see Figs. 8, 9, 10, Z. Kryst., Plate IV, 45, 1908.

Kemter [26] has made a comparison of the etchings of the seven fundamental forms on celestite by means of the solvents HNO_3, HCl, and H_2SO_4. His results were published before the writer's investigation had been completed, and accordingly the following discussion has been necessarily abridged. While there is general agreement in the two investigations, some of the etchings of the writer show differences not recorded by Kemter. These, together with photographs, may be added to supplement the other investigation.

The crystals used for this investigation are from Girgenti, Sicily, and occur as simple, transparent individuals associated with sulfur. The following forms are well developed and reveal distinct etchings: (011), (102), (110).

Dome (011)

The crystals being elongated parallel to the *a* axis, this face is much larger and therefore more desirable for etching. Figures were produced with H_2SO_4, HCl, and HNO_3. Mixtures of these acids were also tried, as well as cold concentrated and hot dilute solutions of each, and good results obtained. If a crystal be immersed for approximately forty seconds in hot dilute HCl, and the (011) face examined, it will be seen to contain many triangular etchings. (See Photo 52.) The figures in the primitive stage of development are usually composed of three faces; a bottom face truncating these may also be present. The figures are very much extended at right angles to the intersection (011)/(001) with the apex turned from this edge. The two longer faces do not form a symmetrical curve of intersection with the crystal face as is noticed on several of the isomorphous carbonates and on (011) of anglesite, but suddenly diverge as

[26] See footnote 27.

they near the base of the figures, producing a break in the contour, which ultimately develops the pentagonal etching to be described later. The third face is much smaller and lies in the zone (011), (001). If solution is allowed to continue, a very noticeable change takes place in the figure; it becomes deeper, its width exceeds the length, and there are five faces which intersect the crystal face in straight lines. The small triangular face of the primitive figure maintains its original position and

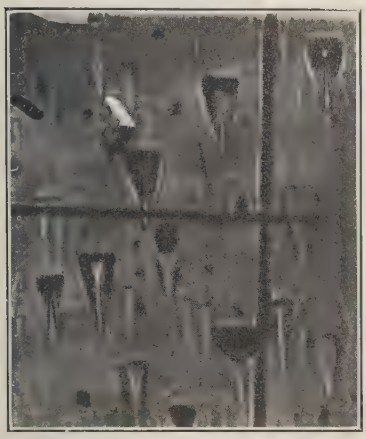


PHOTO 52
Celestite (011), Etched by Dilute Hydrochloric Acid.

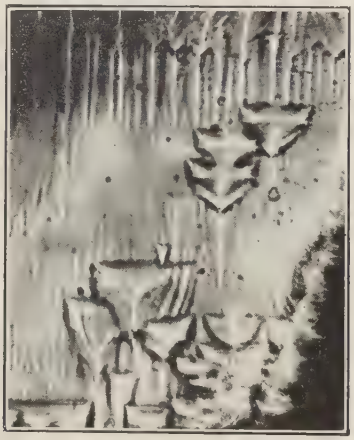


PHOTO 53
Mature Etchings Produced by Boiling Hydrochloric Acid Acting for One Minute on the (011) Form of Celestite.

forms either a curved or straight intersection, with the adjacent faces lying one to the right and one to the left in the broader portion of the figure. For developmental stages see text subfigures a_1, a_2, a_3, a_4, and Fig. 13*A*, the last representing the mature figure. These etchings at certain stages are similar to those of Samojloff and Kemter [27]; the final forms, however, are very different.

If solution is allowed to continue for one minute in boiling HCl the two lateral faces α of a_4 increase very noticeably in size (see upper figure, a_4, and Photo 53). The five faces com-

[27] Ber. Ges. Wiss., Leipzig, **72**, 1920, pp. 56-64.

posing the figure appear to have a similar slope and intersect at a common point near the center of the etching.

If a crystal is placed in cold conc. HCl for a period of fifteen hours' examination shows the dome (011) to be well covered with triangular etchings, oriented as are the figures produced by hot dilute HCl, which they resemble in a small degree. (See Photo 54.) These etchings are not elongated to the extent of those described by Kemter. There is often an indication of a lateral face at either end of the contour forming the base of the triangle; but, this face being so small, the observer is inclined to regard the etchings as flattened isosceles triangles, with the corners rounded at the base rather than pentagonal as are those previously described. Continued solution, however, may accentuate these corner facets. All figures produced by HCl are symmetrical to one vertical plane. Here there is shown a profuse development of beaks leading out from the base of the triangular pits and following a general direction normal to the edge (001) (011). As noted on barite, the beaks are invariably associated with more advanced stages of solution. A drawing of the anomalous type is shown at *b* in Fig. 13*B*.

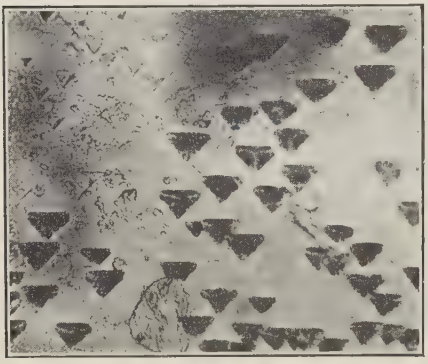


PHOTO 54

Celestite (011), Etched by Cold Concentrated Hydrochloric Acid. Primitive Figures are Visible in the Upper Left Hand Corner of Photo.

The action of HNO_3 on celestite is very similar to that of HCl and the figures bear much resemblance to those produced by that acid. For results of hot dilute HNO_3 acting for two minutes on the face (011), see Photo 55. The manner of development from the simple to the complex figure is quite the same as was observed in the case of HCl, the mature figure resulting from a triangular form. A very similar development

is observed on anglesite with the use of HNO_3; the mature etching, however, is not comparable. The mature HNO_3 figure is composed of five distinct faces, placed in such a manner as to resemble an open envelope. The five contours are straight and sharp, the two at the apex of the figure meeting at an angle of approximately 98°. The figures are elongated vertically. owing

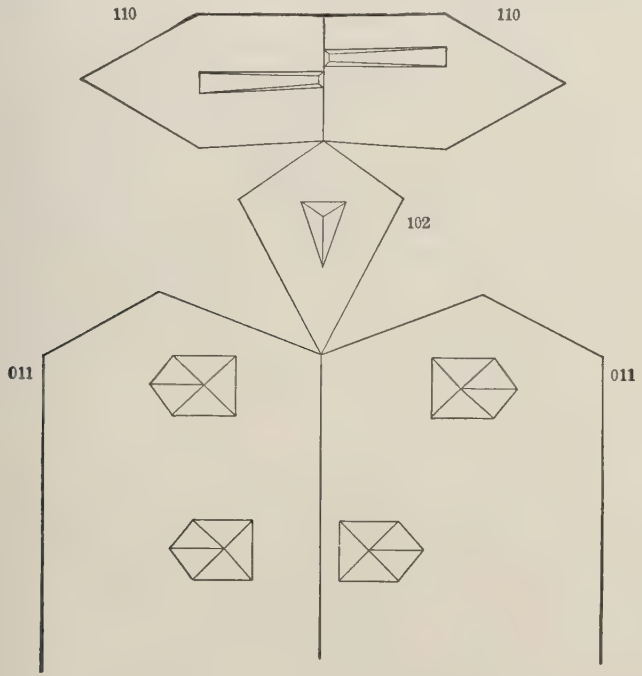


FIG. 13.—Celestite Etched by Dilute HNO_3.

to a greater development of the face α of Fig. a_4, and are also symmetrical to a vertical plane. The less mature figures of the writer are identical with those of Kemter.

By mixing equal parts of HNO_3 and H_2SO_4 and diluting to five times the original volume and boiling, after five minutes' immersion, well-defined figures were obtained. They are quadrilateral and very much extended at right angles to the edge (001)/(011). The two longer contours are curved outward,

while those forming the ends of the figure are short and straight. There are four faces present; those occupying the ends are triangular and are divided symmetrically by a plane passed

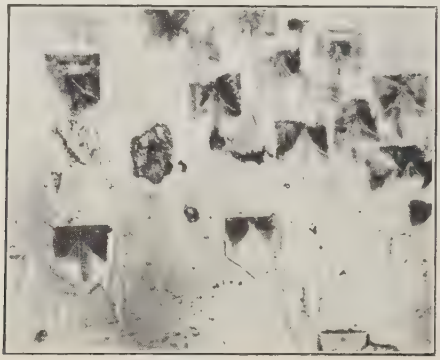


PHOTO 55
Celestite (011), Etched by Hot Dilute Nitric Acid.

lengthwise of the figure. (See Photo 56.) These etchings are unlike either the H_2SO_4 figures of Samojloff or of Kemter, or the HNO_3 figures of the writer.

PHOTO 56
Celestite (011), Etched by a 1 : 1 Mixture of Nitric and Sulfuric Acids.

Photo 57 represents the figures as produced by cold dilute H_2SO_4, after three hours' immersion. They are composed of four faces; the two lying in the zone of the (011) and (001)

forms are of unequal size, consequently the figures are symmetrical to only one plane which accords with the type. These etchings are unlike any reported by Samojloff or Kemter.

Dome (102)

This form etches rapidly with all acids and reveals triangular forms, with the apex turned upward. The etchings produced by dilute HCl, acting for five minutes, are represented in Photo 58.

Photo 57
Celestite (011), Etched by Cold Dilute Sulfuric Acid.

Photo 58
Celestite (102), Etched by Dilute Hydrochloric Acid.

They are characterized by three triangular faces which intersect the crystal surface as straight lines; their symmetry and arrangement of faces may be likened to the (102) figures of barite produced by sulfuric acid; all figures are symmetrical to a vertical plane.

Prism (110)

The prism face is also quite soluble and, if immersed in hot dilute HNO_3 for several minutes, reveals elongated quadrilateral etch figures of simple form and composed of four etch faces having an arrangement symmetrical to an equatorial plane. These figures are similar to those of barite and anglesite when

these minerals are etched under similar conditions, a comparison which may aid in securing proper orientation. The etchings of the three forms, as observed in Fig. 13, indicate the holohedral symmetry of the orthorhombic system.

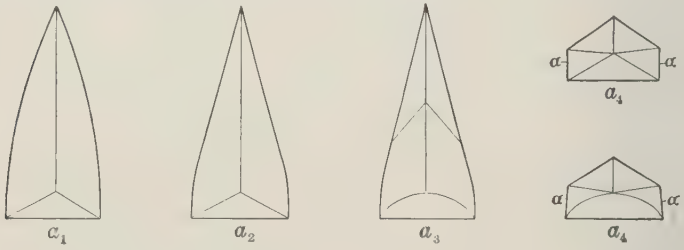


FIG. 13A.—Transitional Changes of the Etch Figures on (011) of Celestite.

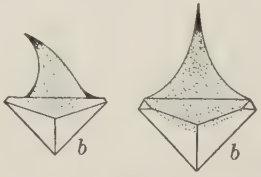


FIG. 13B.

BARITE

This mineral, being one of the isomorphous group, reveals etchings similar in some respects to those of celestite. The etchings as observed by other authors are subsequently described. A very elaborate description of the natural and artificial etchings of barite is given by J. Valentine.[28] The crystals described by him were very clear and tabular parallel to c, possessing the following combination of forms: (001), (110), (102), (011), (010). The base (001) was very often marked by natural etchings; some symmetrical to two planes, others monosymmetrical; occasional basal faces showed striations running parallel to the prism edges in one direction. The prism faces often revealed etch facets measuring (750), (310), and (36 : 35 : 0); other forms measured gave (111). In the zone of the macropinacoid and base he

[28] Z. Kryst., **15**, 1889, p. 576.

observed (905). On crystals from Cornwall, England, he made the following observations: The base (001) is but little attacked while the prism is strongly corroded. The form (011) shows triangular figures oriented symmetrically; the faces composing those lying in the pyramid zone approach the position (22–20–55). On a crystal from Teplitz, he observed large four-sided etchings on (011), which are often marked by striations, parallel to the inclined sides. Large well-defined etchings were observed on the base of barite from Giftberge, near Horsowitz. The figures are rhombic with the longer diagonal parallel to the *b* axis, and composed of four faces corresponding to (2–2–21). On (102) are acute triangular figures with the apex turned to the edge (001)/(102). Artificial figures were obtained by means of the alkali carbonates and concentrated sulfuric acid, the best results being obtained with the sodium solution and sulfuric acid. With the former he obtained, on the base (001), rhombic etchings whose longer diagonal extends parallel to *b*. On the prism (110) he obtained monosymmetrical figures, acute at one end. The figures as produced by hot concentrated sulfuric acid do not differ on the base from those just described. The figures of the prism are quadrilateral, while those of the dome (102) are triangular and symmetrical to a vertical plane. On the whole, the natural and artificial etchings are quite similar.

Tschermak[29] describes artificial etchings on *m* (110) which are pentagonal with the apex turned to the brachyaxis. Becke[30] mentions natural etch figures on (110), which are elongated in the direction of the brachyaxis. Gonnard[31] observed natural etchings on (102) and (011); the former bears triangular figures with apex turned toward the *c* axis; the other dome reveals similar figures, oppositely oriented. Anomalous etchings on (102) are described by Sommerfeldt,[32] and natural figures on (011) are described by Fedorow and Nikitin.[33]

[29] Tschermak, Lehrb. Mineral, Wien, 1881, p. 38.
[30] Fr. Becke, Min. petr. Mitth., **5**, 1883, p. 83; also Z. Kryst., **9**, 221.
[31] F. Gonnard, Z. Kryst., **18**, p. 521.
[32] Z. Kryst., **40**, 4, 13.
[33] Z. Kryst., **34**, 697.

Barite, on account of its anomalous etchings,[34] occasional hemimorphic development,[35] and abnormal pyro-electricity,[36] has at times been identified with a lower symmetry. A study of its etchings by Beckenkamp led him to the conclusion that the crystals were complex intergrowths, and composed of molecules which were asymmetric, their arrangement, however, conforming to the orthorhombic system. Chester described crystals which were hemimorphic parallel to the brachyaxis. Hankel[37] suggested asymmetric development of faces on barite, and Valentine[38] called attention to asymmetric striations on barite from Kronthal. The results obtained by the writer indicate for the most part holohedral symmetry. Anomalous etchings were observed on the base and macrodome, but the writer is unable to see any justification for lower-symmetry classification because of their appearance. The basal face shows a great predominance of bilaterally symmetrical figures, which are similar and of like orientation on opposite faces; this fact, considered with the etchings of other forms, points to holohedral symmetry.

For examination of the artificial etchings of barite, the writer used transparent colorless crystals from Pribram, Bohemia, Austria, and Kremnitz, Hungary. Those of the former locality possess the following combination of crystal forms: *c* (001), *o* (011), *d* (102), *m* (110); those of the latter are simple tabular crystals having only two forms combined, the base (001), and the unit prism (110). The solvents used were dilute cold sulfuric acid, hot concentrated hydrochloric, and hot concentrated nitric, the best results being obtained with nitric and sulfuric acids. Three forms were etched and are described as follows:

Prism (110)

This form, being more soluble, may be definitely etched by nitric acid. The resultant figures are simple, quadrilateral

[34] Beckenkamp, Z. Kryst., **28**, 1897, p. 85.
[35] Chester, Z. Kryst., **14**, 297; also Am. J. Sci., **33**, 1887, 288.
[36] Beckenkamp, Z. Kryst., **44**, 355.
[37] Abh. math.-phys. Cl. sächs. Ges. Wiss., **10**, 280.
[38] *Loc. cit.*, p. 576.

depressions, acute at one end and elongated normal to the vertical axis. (See Fig. 14 and Photo 59.) The chief etch face lies in the prism zone opposite the acute end of the figure. Its slope is so gentle that often the intersection with the crystal face is hardly discernible. At the acute end of the etchings a small triangular face appears, having a much steeper slope and lying in the same zone. The sides of the figure are limited by two equivalent triangular pyramid faces, tapering to a very small angle, where they join the larger face at the surface of the crystal. The figures are oriented, with the broad end turned to the *b* axis, and are monosymmetrical lengthwise.

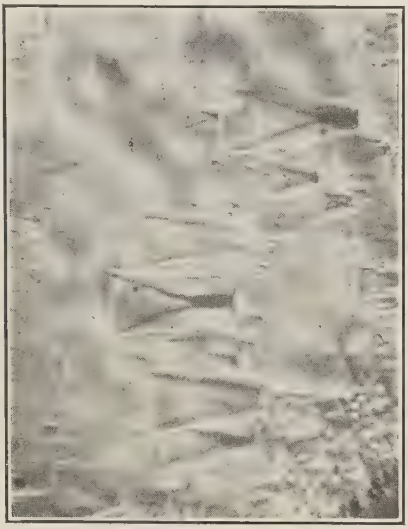


PHOTO 59
Barite (110), Etched by Concentrated Nitric Acid.

DOME (102)

The macrodome, after five minutes' immersion in boiling HCl, becomes well etched with quadrilateral figures having two parallel sides of unequal length with the longer side lying adjacent to the base. The other two sides are symmetrically inclined, hence the figures are divisible by a vertical plane of symmetry. These figures are very similar to those produced by nitric acid, subsequently described. Their position, however, is different. Whether beaks would develop through continued solution is not known, but the figures at this stage show no anomalous growths of any kind.

The figures as produced by cold dilute H_2SO_4, acting for

twenty-four hours, are triangular, with the apex turned toward the brachyaxis. (See Photo 60.) These etchings are similar to those of celestite produced on the same form by nitric acid; the orientation, however, differs. The barite figures often show etched faces within the figures themselves, and when observed in number give the figure a striated appearance parallel to the two equal sides of the triangle. Occasionally the triangular etchings are very shallow, possessing a large bottom face, and this may contain a small triangular pit, similar in shape and orientation to the figure containing it. These etchings are all partcularly impressive because of their simplicity and exceptional distinctness. All the figures indicate the presence of a vertical plane of symmetry.

PHOTO 60
Barite (102), Etched by Cold Dilute Sulfuric Acid. Period of Immersion Was Twenty-four Hours.

By boiling barite crystals for several hours in dilute nitric acid, very distinct etchings may be obtained on (102) and (001). Those of the former may be seen in Photos 61, 62 and 63 and Fig. 14. The first evidence of solution is manifested by the appearance of minute shallow cavities and grooves, which deepen to form mature figures. Their growth is slow with this solvent, but they are at all stages quite distinct and of unusual character. The later development stages result in beautiful anomalies, in the form of beaks and tongues, attached to the deeper central portion of the etchings, extending outward from the longer side. (See Photo 62 and Fig. 14.) The direction of this solution growth is invariably toward the crystal edge (102) (100). However, the tips of these processes may be curved through prolonged action of the solvent. In the incipient stage their

presence is indicated by the development in the deepest portion of the figures of two small faces, whose position approximates verticality with respect to the face (102). (See Fig. 14, *a*.) The etchings, so modified, always possess a black center, as evidence of subsequent beak development, which, in the more advanced stages, appears as *b*, Fig. 14, and Photo 62. The anomalous forms characterize the mature figures. The fact that they are not observed on any primitive etchings supports the suggestion of the writer that beaks are in no manner accidental

PHOTO 61

Barite (102), Etched by Hot Dilute Nitric Acid. Note the Terraced Interior of the Pits.

or due to surface irregularity, but that their origin is directly dependent upon solubility differences inherent within the crystal, which are made manifest under certain special conditions of etching. Anomalous growths of similar nature, produced by the action of hot potassium carbonate upon (102) of barite, are described by Beckenkamp (loc. cit.). Owing to chemical difference of the solvent, the etch figures described by him are unlike those of the writer, and the beaks often extend outward from different parts of the etchings; their manner of development, however, is essentially the same as that of those just described for the solvent HNO_3. The beaks are very numerous; in fact, every mature figure occurring on a large

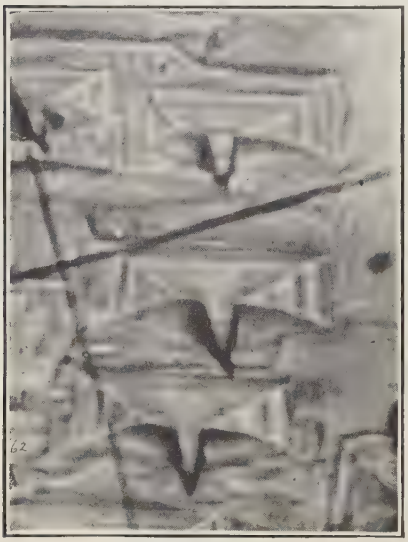


PHOTO 62
Barite (102), Etched by Hot Dilute Nitric Acid. Note Interior Beak Development.

macrodome face of a Pribram crystal was observed to possess this anomaly in some stage of development. No experiments were made to determine what conditions favored such growths, but it may be stated that beaks of this kind were not observed on the prism or brachydome. This observation is in agreement with that of Beckenkamp. That they may occur on the prism, however, is evidenced by his investigations of crystals from other localities.

The etch figure proper is a trapezium-shaped pit, with the longer contours extending parallel to the crystal edge (001)/(102). Often the boundaries are slightly curved, the longer more perceptibly. The mature etchings are beautifully striated or terraced parallel to the outer contours, through internal figure development. Frequently ten or more such steps or striations may be counted in a single pit, and all perfectly symmetrical—the last or deepest terrace yielding to the solution development

PHOTO 63
Barite (102), Etched by Nitric Acid.

described above. These etchings are monosymmetrical parallel to the shorter axis in accordance with the symmetry of the face. The chief etch faces lie in the zone (001 102). The bottom face, so prominent in the early stages of growth, disappears as the

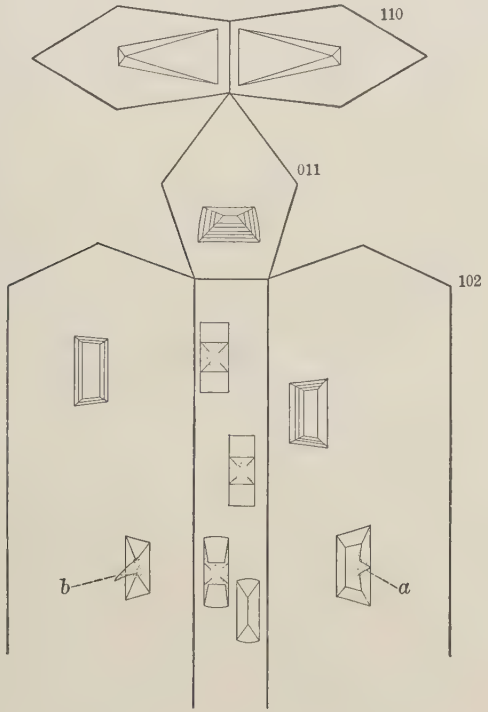


Fig. 14.—Barite Etched by Dilute HNO_3.

figure deepens; its obliteration marks the beginning of beak development.

Dome (011)

This is a much smaller face, and one less commonly observed on the material investigated. Its HNO_3 etchings, however, are analogous to those of (102) but are reversed in position. The striations so pronounced on the (102) etchings are again present in these figures. The arrangement of faces seen in Fig. 14 is

symmetrical to a vertical plane. The delicacy and small size of the etchings have prohibited a more detailed study.

Base (001)

This form, usually present as a definite face, may be successfully etched by any of the common laboratory acids. If allowed to lie for a period of four or five days in cold dilute sulfuric acid, the basal face becomes covered with shallow rectangular forms composed of four triangular faces occupying the dome zones. (See Photo 64.) The chief etch faces lie in the zone (001)/(011) normal to elongation. These figures are perfectly symmetrical over the entire face, an absence of anomalous forms being conspicuous. It is admitted, however, that these etchings represent an intermediate stage of development, solution having been discontinued here to prevent intergrowth. Further development of the figures may show irregularities, but certainly they accord with holohedral symmetry when developed to this stage.

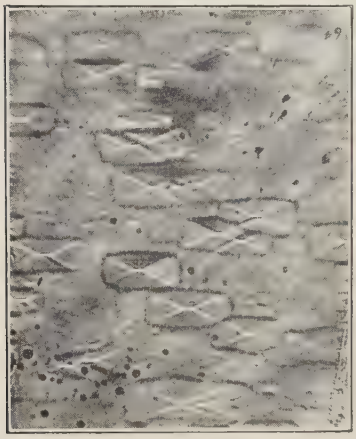


Photo 64
Barite (001), Etched by Cold Sulfuric Acid, after Several Day's Immersion.

A barite crystal from Kremnitz, Hungary, after being immersed in boiling hydrochloric acid for five minutes, also gave distinct etch figures on the base. These are more elongated and deeper than those produced by sulfuric acid; their orientation and symmetry, however, are the same. There is great resemblance between the hydrochloric acid figures and those produced by hot concentrated nitric; but with the latter acid two or three different kinds of etchings were observed on the basal cleavage plates of this mineral. Among these there is

represented a single anomalous figure of the polar type, which very evidently is a beak development of an end face of a rectangular etching. (See Photo 66.) The conical solution tube can be observed attached at one end of the rectangular pit. That there are no more, is probably due to insufficient solution, as it has become very evident that many of these solution beaks are confined to definite developmental stages and are often late in appearing. Especially is this true of the normal solution beak which selects for its point of attack a pit or deeper corner of the figure, from which it often strikes directly toward the interior of the crystal.

Photo 65
Barite (001), Etched by Hot Nitric Acid.

The principal types of basal etchings produced by hot nitric acid are shown in Fig. 14. Those with black centers usually develop more rapidly upon the exterior basal face, while the simple rectangular form develops most rapidly on interior cleavage plates. The latter, having a very fine surface, are more resistant to attack; consequently, a cleavage fragment possessing one exterior crystal surface shows the more mature figures upon this face. Interrupted etching confirms this, as it is readily observed that the etchings possessing the black centers are derivatives of the elongated simple form, both being truly symmetrical to two planes at right angles in accordance with holohedral symmetry.

The nitric acid figures are unusual and warrant special mention. After a small crystal has been immersed in hot nitric acid for a considerable period (four hours), microscopic examination shows the exterior basal plane to be covered with

black square or rectangular pits, the bottom of which is not visible. (See Photo 65.) However, that these black pits are limited by definite plane faces with symmetrical arrangement may be observed when the crystal is mounted and placed upon the microscope stage in a darkened room where a beam of bright light is permitted to strike the upper surface of the slide. By rotating the stage these small facets, under high magnification, can be seen to flash periodically. Often their shape can definitely be determined. These faces possess a very steep slope, often approaching verticality. Usually they are four in number, arranged in pairs, often of different slope and shape. The pair of faces lying parallel to elongation of the figure may be continuous at either end, where their intersection with a large flat face lying without the pit gradually slopes upward to the surface, where it forms a very acute angle. In view of the uncertain and indefinite end contours of the two larger etch facets containing the pit, the steep side faces give the etching an H appearance. (See Photo 65.) These may be seen in great number during the etching process, and although the development is most unusual, it corresponds to the symmetry of the face. It is evident that solution proceeds with greater rapidity parallel to *b*. Attention has been especially directed to etchings of this character by Beckenkamp, in connection with both barite and aragonite. However, the anomalous etchings observed by the writer during the examination of barite were, to all appearances, similar in origin to those observed on other minerals, and, because of the

PHOTO 66
Barite (001), Showing Conical Solution Tube Developed by Hot Nitric Acid.

frequency with which these beaks are met during etching investigation on high-symmetry forms, their asymmetrical character must not be alone relied upon as indicative of lower-symmetry classification for the crystal. Disregarding this abnormal type of etching, barite conforms to the holohedral symmetry of the orthorhombic system.

ANGLESITE

Slavik [39] has described natural etchings on the (001) and (110) forms of anglesite, which correspond to orthorhombic holohedral symmetry. Von Lang [40] suggested bisphenoidal symmetry. Samojloff [41] has described natural etchings on the (102) and (001) forms of anglesite, and also artificial figures developed on (011), (102), and (001) by means of nitric acid and sodium carbonate. The figures produced on (011) by both solvents reveal no distinct differences either in shape or in orientation. All figures favor holohedral symmetry. The sulfates of Ba, Pb, and Sr, according to Samojloff, yield etching figures which are similar in orientation, excepting those produced on the (011) form of barite and celestite when treated with alkali carbonate. The writer's results as obtained with HNO_3 show considerable variation, especially on (102).

Owing to scarcity of suitable material, the results of the anglesite etchings are not as complete as was hoped for; but in view of the very limited attention previously given the etch figures of this mineral, the following description may be of value.

A few of the smaller ice-clear Monte Poni (Sardinia) crystals were treated in hot dilute NHO_3, and in 10 cc. of cold water to which had been added half a dozen drops of conc. HNO_3. Immersion in the former solvent for two minutes was amply sufficient for etching; in the latter the crystals were allowed to lie over night.

A crystal, when treated with hot HNO_3, becomes beautifully

[39] Z. Kryst., **44**, 1908, p. 83.
[40] Sitzber. Akad. Wiss., Wien., **26**, 1859, 276.
[41] Z. Kryst., **45**, 1908, p. 122.

etched, with the best-developed figures occurring on the forms (011), (110), (100), (102); other forms present, such as pyramids and the base, do not respond to the solvent so satisfactorily, although the base (001), not well developed on these crystals, did reveal a few distinct etchings. One of the pyramids becomes dull. The prism appears to be the most soluble and very soon reveals intergrown etchings.

PHOTO 67
Anglesite (011), Etched by Hot Dilute Nitric Acid.

PHOTO 68
Anglesite (011), Etched by Cold Dilute Nitric Acid.

DOME (011)

This face practically always yields distinct etch figures, even with varying concentrations, the only noticeable change in the shape of the figure being that of shortening or elongation; the orientation remains the same. These figures as obtained with hot dilute HNO_3 may be seen in Photo 67. In cold dilute HNO_3 they are as in Photo 68. The transitional changes from primitive to mature figures are always very evident, and, as is so often observed on other species, age causes greater depth,

with some tendency towards straightening of the contours. The primitive figures are always visible as exceedingly shallow depressions, triangular in shape, with the two longer contours curved and meeting at the acute end of the pit to form an angle of approximately 60°. The bottom face is dominant, being limited by very narrow margins, which gradually develop in length and width until in the mature figure the bottom face is entirely obliterated, and the etching first formed is consequently deeper, more elongated, and composed of three definite facets which intersect symmetrically. (*Cf.* Figs. *a* and a^1 in Fig. 15.) The elongation is normal to the edge (001)/(011), with the acute angle of the figures turned from the basal pinacoid. No anomalous etchings of any kind were observed upon any faces of this form, and the figures by their shape indicate a plane of symmetry through *b* and *c*, and by their positions on all faces of the form, two other axial planes of symmetry at right angles. This conforms to the holohedral symmetry of the orthorhombic system.

If immersion is continued for a period of several hours, in the more dilute solvent, the figures of this form pass through similar evolutionary growth, but the figures at all times are broader and much less elongated. They are composed of three faces, so arranged as to be symmetrical to a plane as are those just described, but the end facet of these figures intersects the longer faces in two definite straight lines, the angle between which is approximately 128°. Similar measurements on the figures produced by the other solvent gave approximately 80°; both values, however, are average, as this angle was observed to vary slightly. All figures by both solvents conform to expected symmetry at all stages of growth.

Dome (102)

The etchings of this form are always very definite, simple quadrilateral pits which deepen as solution continues. The primitive form again contains a bottom face which is obliterated through substitution of side facets. The mature etch figure is composed of four triangular faces slightly elongated at right

angles to the vertical axis and turned with the broader side adjacent to (001). The figures are monosymmetrical with the chief etch faces lying in the zone (102) (001). This face is usually well developed, but slightly striated vertically. The etch figures developed by hot dilute HNO_3 are definite and simple in arrangement of faces, as may be seen from Fig. 15.

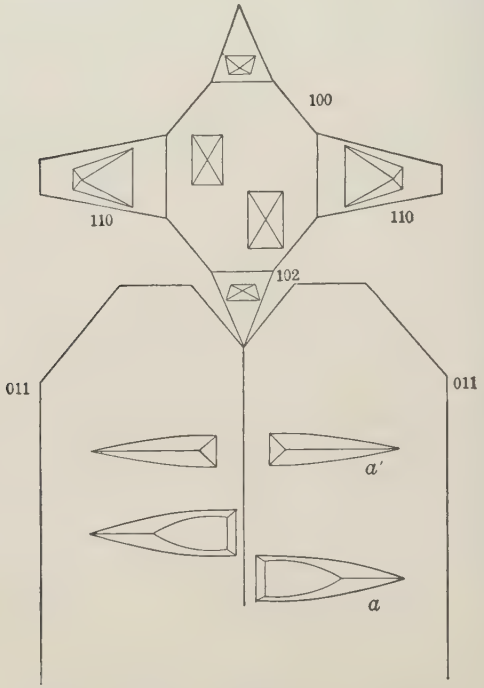


FIG. 15.—Anglesite Etched by Dilute HNO_3

They are rectangular, slightly elongated parallel to *c*, and composed of four triangular faces meeting at a central point which forms the pit of the figures. The immature etchings, like the others of this mineral, usually possess a plane lying parallel to the crystal face; but this soon vanishes as solution continues. The chief etch facets lie in the prism zone; the subordinate faces lie in the zone of the macrodome. The figures are thus conformable to two planes of symmetry at right angles. When the

weaker solvent is used, the figures of this face are rotated through 90°. They are slightly more rounded and elongated, and extend in a direction across the striations, 90° to the vertical axis. Hence, the chief etch faces for the weaker solvent are normal to those of the hot dilute nitric acid.

Prism, (110)

Definite etchings may be obtained on this face after very brief immersion in hot HNO_3. They are composed of four faces, two of which are of the prism zone, the other two of the pyramid zone. The figures are quadrilateral, bounded by straight contours and elongated parallel to the crystal edge (111/110). The unlike development at the ends of the etchings reduce their symmetry to one plane, that containing the crystallographical axes *a* and *b*.

The base, while usually a narrow face, possesses very few surface irregularities, and consequently may be successfully etched if cautiously treated with hot dilute HNO_3. The etchings as obtained on a single face of this form are of two kinds, one the outgrowth of the other. The primitive figures are typically spindle-shaped and apparently without depth, so prominent is the bottom face. The mature figures, being modifications, assume more definite limiting planes, usually four in number and symmetrical to two planes at right angles. The elongation of the basal etchings is parallel to the *b* crystallographic axis, and agrees with the results of Samojloff.

The pyramid faces, occasionally well developed, are variants in their reaction to the solvent. The best-developed form, probably the unit pyramid, remains bright and yields small but definite figures which are asymmetrical and triangular. Their arrangement on the four faces at the termination of the crystal is in accordance with the etchings of other forms.

Thus, from the etching experiments above described, anglesite is symmetrical to three planes in accordance with the holohedral class of the orthorhombic system.

TOPAZ

In view of the fact that a detailed study of the etching figures of topaz has not been attempted, and in consequence of doubt expressed by certain authors as to the holohedral character of this mineral, the results of a careful examination of the etchings of the fundamental forms may be of interest. Baumhauer [42] was able to obtain distinct figures on the base and unit prism of Brazilian topaz, by means of potassium hydroxide. The base figures are rhombic and oriented with the sides parallel to the edge (001/110). They are usually composed of four faces so placed as to be divisible by two symmetry planes, which accords with the holohedral class. The prism faces are marked by many quadrilateral depressions, elongated in the direction of the *c* axis, and divisible by an equatorial plane of symmetry (also indicating holohedrism).

E. S. Fedorov [43] described natural etchings occurring on topaz crystals from Alabaschka and Urulga, the description being illustrated by seven large photographs. He observed the following: constancy in the type of etch figures occurring on equivalent faces; the presence of two kinds of figures, that is, a formation of etch figures on faces, which have arisen through etching; and a very noticeable difference between the etchings of different crystal forms. References to work on the etching of topaz, by Goldschmidt and Rosicky, have been seen, but the original article has not been accessible to the writer.

Owing to the abundance of suitable material obtained from the Thomas Mountain locality, in Utah, little difficulty was experienced in selecting clear brownish crystals which were very satisfactory for the purpose of etching. Although six fundamental forms are common in this locality, the seventh, the macropinacoid (100), is apparently always wanting; the extreme rarity of this form was not really appreciated, until a diligent search through the Princeton Museum specimens, coming from a variety of localities, failed to reveal a single crystal bearing this face.

[42] Neues Jahrb. Min. Geol., 1876, 5.
[43] Ann. Inst. Mines, **1**, 1908.

Topaz, being a very insoluble mineral, is little attacked by acids; consequently, fusions similar to those which have been used for etching tourmaline were employed for the investigation of the topaz etching figures. Potassium hydroxide, if concentrated, was found to corrode the crystal, so that a more dilute

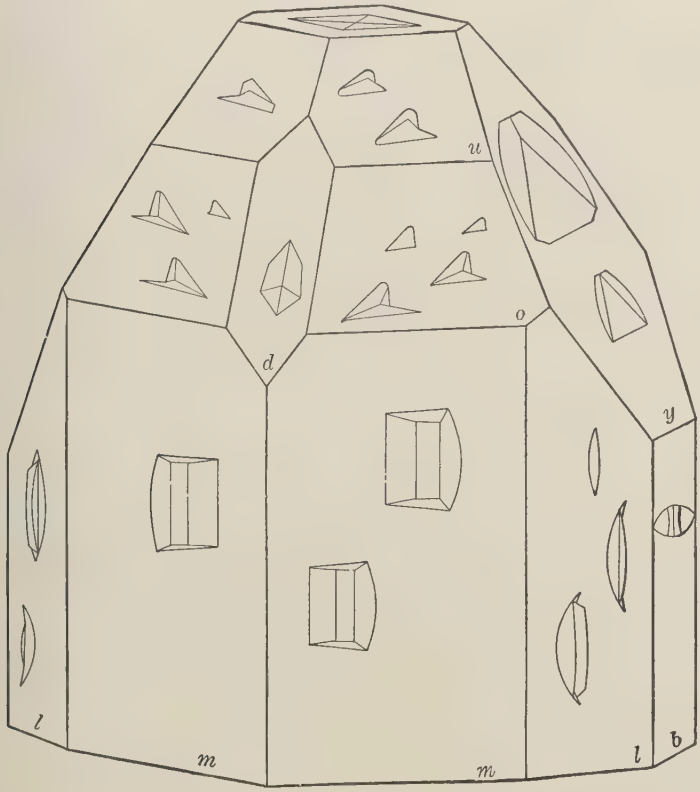


Fig. 16.—Etch Figures on Topaz.

fusion was prepared by adding a little water; as this solution becomes more and more concentrated the crystal is attacked quite readily, the six forms revealing figures as seen in Fig. 16, where the holohedral symmetry of the orthorhombic system is demonstrated.

Unit Prism (110)

Several minutes' immersion in the potassium hydroxide fusion produces distinct etchings on this form. (See Photo 69.) They are for the most part composed of five faces in the mature stage of development and are slightly elongated parallel to the prism edges. The primitive figures are usually semicircular but have very little relief; consequently, if there are lateral faces present at this stage of growth, they are microscopic.

Photo 69
Topaz (110), Etched by Potassium Hydroxide Fusion.

The mature figures are generally quadrilateral in outline, although either of the two longer boundaries may be modified at the ends by two short straight lines. These longer boundaries may be curved or straight. The ends of the figures are similarly developed, being limited by a short straight line inclined to the prism edge at an angle of approximately 85°; thus the figures are symmetrical to an equatorial plane.

If a red-hot fusion of potassium bisulfate and powdered fluorite, mixed in a proportion of three to one, is allowed to act upon topaz for a period of forty minutes, the unit prism presents an appearance not unlike that of the potassium hydroxide fusion. The figures, however, are more rectangular in outline, and composed of four or five faces accordingly as the figures are mature or primitive. (See Photo 70.) In the mature etchings, the four bounding faces are usually triangular and meet at a point well to one side of the figure. Like the figures previously described,

the two larger planes lie in the prism zone, hence the etchings are elongated parallel to the prism edges, and although the contour at first appears symmetrical in two directions, closer examination reveals two faces lying in the prism zone which are not of of the same intercept. The ends of the figure above and below

PHOTO 70
Topaz (110), Etched by Potassium Bisulfate–Fluorspar Fusion.

are similarly developed; consequently, the etchings indicate an equatorial plane of symmetry.

PRISM (120)

This form is usually more or less striated, so that the etching is likely to proceed too rapidly, unless precautions are used. Nevertheless, the two solvents used for the previous etchings gave equally good results upon the prism *l*. The etch figures produced by four minutes' immersion in a dilute fusion of potassium hydroxide are represented in Photo 71. They are oval figures, acute at either end and elongated parallel to the prism edges. Of the two longer contours, the one adjacent to

edge (110 $\bar{1}$20) is more sharply curved, indicating the absence of a vertical plane of symmetry. As solution continues the ends of the figures become modified through the continuation of the larger face as a pointed appendage. This may be seen in Fig. 16, which, in the most mature stage of development, marks the intersection of a small triangular face with the surface

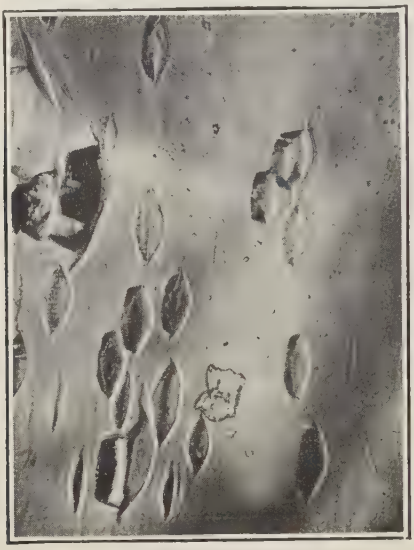


Photo 71
Topaz (120), Etched by Potassium Hydroxide Fusion.

of the crystal. It is surprising what a change from simplicity to complexity takes place in the evolution of the etch figures as solution goes on; but never at any stage does the etching fail to meet the symmetry requirement of the prism face, which in this case consists of an equatorial plane of symmetry.

Photograph 72 represents the etchings produced on the prism (120), after immersion in the potassium bisulfate and fluorite fusion for forty minutes. These figures are very similar to those just described in the mature stage, but in the earlier stages of development the pointed appendages, so prominent on the KOH figures, do not appear to be present. However, a profusion of

normal beaks may be observed leading out from the deeper portions of the mature etchings. (See Fig. 6.) These etchings are fan-shaped, with three distinct faces grouped about one side of the central portion of the figures. Opposite these there lies a large face which descends gradually from the crystal surface to the deeper portion of the figures, and the contour of which is a

PHOTO 72

Topaz (120), Etched by Potassium Bisulfate–Fluorspar Fusion. The Dark Central Portion of the Figures Indicates Beak Development (cf. Fig. 6).

symmetrical curve. The figures, although very complex, are symmetrical above and below the equatorial plane.

BRACHYPINACOID (010)

Although the brachypinacoid is frequently present on the Thomas Mountains crystals, the face is usually small and reveals only a few well-defined etchings. (See Photo 73.) The figures are simple elliptical forms with the elongation parallel to the *a* axis; they are usually composed of four faces symmetri-

cally arranged in pairs, with a groove running through the center of the figures, parallel to the short axis of the ellipse. In accordance with the type they indicate two planes of symmetry, one passing through the *b* and *c* axes, the other the equatorial plane. Hence, the various etchings of the prism zone are alike, in that they are all symmetrical to an equatorial plane.

PHOTO 73
Topaz (010), Etched by Potassium Hydroxide Fusion.

PYRAMIDS

The pyramids (221) and (111) are well developed and yield very fine etchings after only a brief immersion in the potassium hydroxide fusion. (See Fig. 16.) The figures occurring on (221) are simple triangular pits, usually composed of three faces, asymmetrically arranged. The figures are elongated in a direction inclined to the edge (221/110), with the acute end turned toward the macrodome. The base of the triangles is often continued, producing a pointed appendage or surface beak at the larger angle of the figures. (See Photo 74.) The etchings by their positions on adjacent faces indicate two vertical planes

of symmetry in the crystal, but the pyramid faces, as indicated by the form of the etchings, possess a molecular configuration which is asymmetrical.

The unit pyramid behaves very similarly to the (221) form and the figures are only slightly different. (See Fig. 16 and Photo 75.) They have a similar orientation and are asymmetrical; they are also much more elongated, possessing curved boundaries, and being rounded at the acute angle. Here, however, the beaks are more accentuated than those of (221). Like the etchings of (221), their position on adjacent pyramid faces indicates the presence of two symmetry planes.

PHOTO 74
Topaz (221), Etched by Potassium Hydroxide Fusion (cf. Photo 75).

PHOTO 75
Topaz (111), Etched by Potassium Hydroxide Fusion.

DOMES

Of the two domes present (201) and (041), the brachydome is usually better developed and is acted upon by the alkali fusion more rapidly than the other form. Immersion in dilute potassium

hydroxide fusion for a time sufficient to corrode the brachydome, produced only a few small etch pits on the macro form. This difference of solubility is not so marked in the case of the potassium bisulfate-fluorite fusion. It is to be observed, however, that such a comparison of the relative solubilities of the two forms can be made only when both faces are of like perfection, for often a more insoluble form is very readily attacked by solvents, because of an imperfect or rough surface. The great

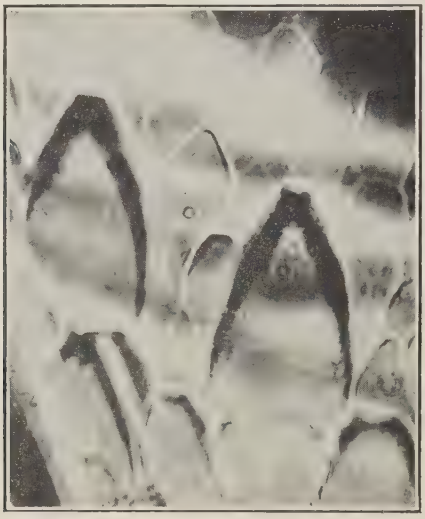


PHOTO 76
Topaz (041), Etched by Potassium Hydroxide Fusion.

necessity of a perfect crystal surface for the investigation of artificial etchings cannot be overemphasized.

Well-defined etchings were obtained on the macrodome after several minutes' immersion in a dilute fusion of potassium hydroxide. The figures, although small, appear as illustrated in Fig. 16, Form *d*. They are composed of three or four faces, and are usually hexagonal, broader at the lower end and elongated vertically. The figures are symmetrical to a vertical plane.

The brachydome etches with great ease if immersed in either of the two fusions. The figures produced by potassium hydroxide

are illustrated in Fig. 16, Form *y*. There are present three faces, the largest of which is triangular and lies in the zone of the brachydome and base. At either side there is a narrow curved face which extends the entire length of the figures, and these, meeting, form the acute apex of the triangular etching figure. (See Photo 76.) The figures have curved contours and are oriented symmetrically, with the apex turned upward. Different etchings were obtained with the potassium bisulfate-

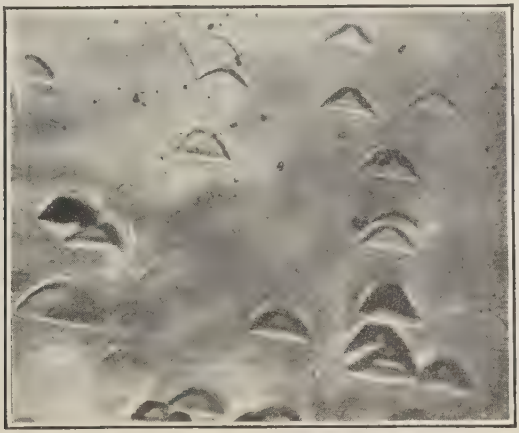


PHOTO 77

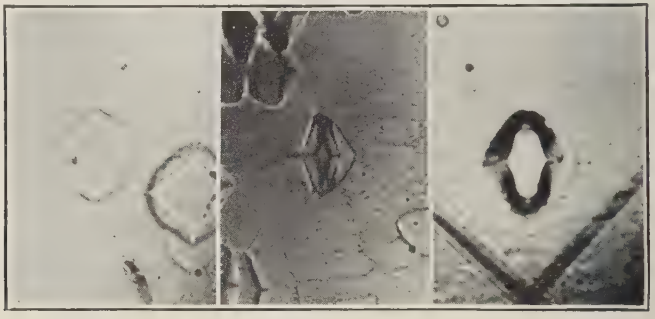
Topaz (041), Etched by Potassium Bisulfate–Fluorspar Fusion.

fluorite fusion, a longer immersion, even to the extent of thirty minutes, being necessary; but the figures produced are usually distinct (see Photo 77) and are of two kinds, triangular and semi-circular; the former may appear flattened, due to the truncation of the apex by a small face lying in the zone of the brachydome. Occasional figures are marked by faces lying at the bottom, but this represents a particular stage in the development. The contour forming the base of the figures is straight and extends parallel to the intersection (041 010). The other boundary lines are curved, but are symmetrical, revealing a vertical plane of symmetry through the face. Hence the dome faces, as repre-

sented by their etching figures, are also in accordance with the holohedral symmetry of the orthorhombic system.

Base (001)

This form etches very rapidly with the potassium hydroxide fusion and, as the etchings produced do not differ from those described by Baumhauer, either in form or orientation, no further description is required. If a crystal is immersed in a red-hot fusion of potassium bisulfate and powdered fluorite for



a *b* *c*

Photo 78

Topaz (001), Showing the Evolution of Etch Figures as Produced by Potassium Bisulfate-Fluorspar Fusion.

about twenty minutes, the figures resulting are quite unlike any hitherto described on topaz. The figures as they first appear are to a considerable degree circular, with a very slight elongation parallel to *b*. (See Photo 78, *a*.) As solution continues the figures become deeper and angular (see Photo 78, *b*); they become rhombic forms, the diagonals of which appear to be approximately of the same length; the contour is still rounded to a small degree and remains so, the continued development being one of complexity, and confined to the inner portion of the pit. (See Photo 78, *c*.) This development as observed under greater magnification includes the formation of a long rhombic pit within the primitive figures and elongated parallel to *a*; each side of this rhombic form is subdivided into two faces, as the mature stage

approaches, producing as the ultimate form, Photo 79, an etching bearing the primitive outline inset with an elongated octagonal pit, extending parallel to the brachyaxis and divisible by two symmetry planes. This manner of growth, while involving a great many changes, never alters the figure to a form other

PHOTO 79

Topaz (001), Showing an Enlarged Reproduction of Photo 78*c*.

than one that accurately indicates the symmetry of the basal pinacoid.

Topaz is, therefore, according to the etchings of six fundamental crystal forms, divisible by three symmetry planes at right angles, which accords with the holohedral symmetry of the orthorhombic system of crystals.

CHAPTER VII

SUMMARY AND CONCLUSIONS

The Etch Method, during its development over a period of nearly a century and a quarter, has been a subject of fascinating interest to many prominent investigators. From its very beginning in 1808, with the experiments of Widmannstätten, to the culminating work of Baumhauer published nearly a century later, and also in other important contributions of subsequent date, great reliance has been placed upon the Etch Figure as a determinant of crystal symmetry. The readiness with which the Etch Method may be employed, in connection with the validity and magnitude of results obtained, has been chiefly responsible for its development. Examples, such as the tetartohedral willemite and dolomite, the hemihedrism of the rhombohedral carbonates, the apatite group, wulfenite, and others, may be cited to show the decided advantage of this method over optical and crystallographic means of investigation. The various thirty-two crystal types cannot be differentiated by optical means, except in the rare holoaxial classes, and in these only when they are considered in connection with non-metallic species. The identification of type may not always be possible by crystallographic means, for the most general form, which is usually the rarest, may not be developed in combination with other holohedral forms whose molecular configuration of lower symmetry is not evident.

Etch figures, however, may be employed to indicate specifically to which crystal type a mineral belongs, and the information desired is always more easily obtained from common and important faces than from rarer forms of a lesser reticulate density. Since these important faces are usually prominent cleavage

directions, the absolute necessity of having faultless crystals is thereby obviated, for it has been repeatedly stressed that, for etching, cleavage surfaces are often far superior to exterior crystal faces. Moreover, the development of the etchings of any mineral is not restricted to the use of a single solvent, for, through employment of many solutions of varying concentration and chemical constituency, the etchings of a given crystal form remain as symmetry invariants. This is a fact of great advantage when applying the method, for it not only serves as a check upon one's symmetry interpretation, but also points conclusively to a direct relationship between the etch figure and molecular forces within the crystal. The following facts serve to substantiate this conclusion: that corrosion remnants of crystals are often found bounded by definite etch facets; that etch figures of exceptional size and perfection are often observed; that etch faces arrange themselves in definite crystallographic zones; that a crystal face completely removed by solution may often be again etched with definite figures; that internal cleavage planes may react with the solvent to produce etch figures of exceptional size and perfection, identical with those at the crystal surface; and lastly, that one etch figure may develop within another, penetrating to a depth of $\frac{1}{2}$ mm. Many cases may be cited to show agreement in the results obtained by the X-ray and the etch methods. The author's investigations of the etchings of such minerals as calcite, siderite, rhodochrosite, smithsonite, magnesite, cuprite, beryl, topaz, apatite, tourmaline, phenacite, and others have all been confirmed by the X-ray studies of these minerals by other investigators. Dr. Wherry [1] regards crystals as being so constituted that the surface layers of molecules are undersaturated with respect to valence, i.e., have free bonds leading out from the crystal face, the symmetry of which may be different from that shown by molecular layers deeper within the crystal. This suggestion may help to explain certain phenomena sometimes observed during etching, namely, the momentary development of peculiar anomalous solution pits which may lead to misinterpretation. These immature etchings,

[1] Personal correspondence.

however, through continued solution, become well-developed figures of definite symmetry. Hence, it would seem that this surface influence does not permanently distort the etching. As evidence of this the writer would call attention to the rather extensive etching experiments which he has performed involving the study of twenty-two different minerals, representing ten symmetry classes. Over fifty different crystal forms were investigated by means of more than one solvent, and most of them by means of at least three solvents of different chemical constituency, giving rise to a large number of cases where the symmetry might be revealed by etching phenomena; and in all of these cases the expected symmetry resulted. It would seem, then, that etch figures, when carefully produced on homogeneous substances and properly interpreted, are capable of showing crystal symmetry. If there are cases where these other influences prevent the true symmetry from being revealed in mature figures, such cases are probably rare, in the opinion of the writer.

It has been shown that etch figures may determine the crystal type to which a given crystal belongs. They may also indicate the presence of twinning, often in its most intricate form, as evidenced in the etching of leucite, boracite, dolomite, quartz, and other minerals. By a comparative study of etching phenomena, the chemical relations existent among the members of certain mineral groups, as well as their relative solubilities, may become apparent. In the absence of cleavage, peculiarly distorted crystals may be properly oriented by a study of their etchings.

At all times, however, the etching itself, as well as its orientation, must be carefully studied in order to discriminate between typical and anomalous forms, which are commonly present on the same crystal face, and which are often a source of misinterpretation. One phase of this type of solution is evidenced in the so-called beaks, which may occur in three forms: the crack beak, the normal beak, and tubular beak. These, as has been shown, may be developed on almost any crystal under special conditions of etching, and are apparently subject to chemical control, for

by change of solvent the character of the beak may be altered or the beak eliminated entirely. As an illustration of the former change, the (120) prism of topaz treated with $KHSO_4$ plus CaF_2 fusion may serve as illustration. When the potassium bisulfate-fluorspar fusion was employed, the crack beaks so prominent on KOH etchings of this form disappeared, and in their stead beautiful normal beaks were developed in profusion. As an illustration of complete elimination of the beak, calcite may be cited; in this case the change from hydrochloric to citric acid resulted not only in beak obliteration, but also caused a great change in the direction of elongation of the etchings. Different explanations are offered for the appearance of beaks, and it is claimed that they are not the result of foreign admixture or any fortuitous cause, but rather a normal solution process which appears under special etching conditions, often associated with more mature figure development, and one which may just as readily occur in chemically pure as in contaminated crystals.

Transitional changes in the etch figure may result during certain stages of growth, in forms of variable symmetry. This fact suggests the necessity of caution upon the part of those employing the Etch Method. As a consequence of this it follows that a given crystal face may, under identical conditions of etching, reveal different figures, the shape of which may often be influenced by age. Minerals such as topaz, apophyllite, celestite, barite, anglesite, beryl, and others, are cited as evidence of this evolutionary change which accompanies the development of etch figures.

It is also concluded that the distribution of etch figures upon a crystal face is often due to differential solution arising from surface irregularities, and is not in all cases dependent upon "regions of weak attachment" within the crystal. Evidences of the soundness of this conclusion are given.

From a consideration of the data respecting the importance of the etch figure in isomorphism, it is concluded that this matter is not definitely settled, owing to the dearth of quantitative experimental work, and to lack of standards or limits of variation by which the results of such investigations may be measured.

Much of the work of Baumhauer and Daly favors a relation between isomorphous compounds and similarity of etchings, but certain departures from this relation have been observed. The converse, that similarity of etch figures indicates isomorphous relation, is held by Retgers to be invalid. The writer's work on rhombohedral carbonates and on the orthorhombic sulfates would suggest that the degree of similarity shown by the etchings may vary with the form, if not also with the solvent.

As an example of the application of the etch method, a detailed account of the etch figures of several important minerals is given. Included among these are those of topaz, apophyllite, cuprite and wulfenite, whose symmetries have been questioned. The etchings of the first three of these indicate holohedrism; the fourth conforms to pyramidal hemihedrism.

The nature and development of the etch figure have now been considered, and its importance as a symmetry determinant exemplified. There has not, however, been sufficient quantitative study of the etch method, or sufficient coöperation among different investigators, nor has there been adequate study of the etch figure itself, to permit the etch method to assert its real value in mineralogical investigation; and until such researches become the object of a greater number of careful investigators, it is to be expected that the results obtained by etch figures may not in all cases agree.

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